2,3-DIPHENYLBUTADIENE

2,3-DIPHENYLBUTADIENE

A Thesis

by

Charles G. Eliot, B.Sc.

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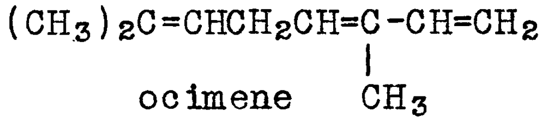
HISTORICAL INTRODUCTION

The conjugated diolefinic hydrocarbons have formed the subject of many investigations during the past forty years. This has been on account of the increasing commercial importance of a few such compounds in the manufacture of synthetic rubbers and similar polymers, and the utilization of by-products of the petroleum and coal-tar industries. In this way much information about the properties and reactions of 1,3-butadiene, isoprene, chloroprene, 2,3-dimethylbutadiene-1,3 and 1,4-diphenylbutadiene-1,3 has been accumulated.

The subject of this thesis, 2,3-diphenylbutadiene-1,3, has not been studied to any great extent; but, before dealing with this compound in detail, the general reactions of the conjugated dienes will be considered (4,5).

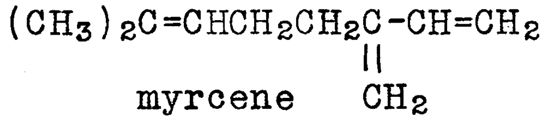
Occurrence and Preparation.

While some of these hydrocarbons, such as the terpenes ocimene and myrcene,



$(CH_3)_2C{=}CHCH_2CH{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2$

ocimene



$(CH_3)_2C{=}CHCH_2CH_2\underset{\underset{\displaystyle CH_2}{\|}}{C}{-}CH{=}CH_2$

myrcene

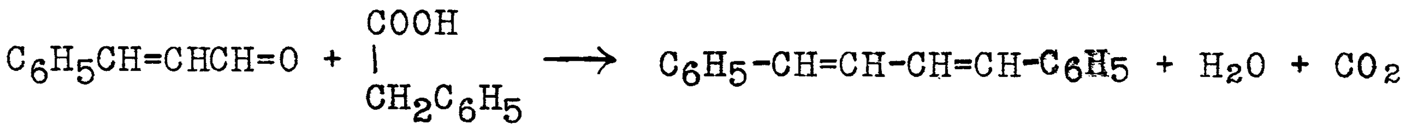
and the carotenoid hydrocarbons (6), occur in nature, and while several of the simpler members can be prepared by the pyrolysis of oils and petroleum, most members of this group must be prepared synthetically. The methods used are generally special cases of those elimination reactions used to prepare ethylenic compounds.

A common method is to eliminate the elements of water from a suitable glycol or unsaturated alcohol. This is usually carried out by heating in the presence of a dehydrating agent or catalyst. This method of preparation is often the most convenient, as the starting materials are generally easy to synthesise. In many cases elimination can take place in more than one way and a mixture of isomers is obtained.

Similar methods include the removal of the elements of hydrogen halide from suitable dihalides or unsaturated monohalides by basic reagents; and elimination, by means of zinc, of two atoms of halogen from suitable tetrahalides or unsaturated dihalides. Exhaustive methylation of suitable dialkylamino compounds will also yield conjugated hydrocarbons.

Dienes are also formed by pyrolytic decompositions of hydrocarbons and alcohols. The yields from these methods are low, but the cheapness of the starting products makes some of them commercially important. Turpentine, fusel oil and the lower aliphatic alcohols can be used in these processes.

Most conjugated systems, especially the longer polyenes (1), can be obtained by a suitable aldol condensation. For example (1,2):



$$C_6H_5CH{=}CHCH{=}O + \underset{CH_2C_6H_5}{\overset{COOH}{|}} \longrightarrow C_6H_5\text{-}CH{=}CH\text{-}CH{=}CH\text{-}C_6H_5 + H_2O + CO_2$$

$$n(CH_3CH{=}CHCHO) \longrightarrow CH_3CH({=}CHCH{=}CHCH{=})_n\ CH\text{-}CHO.$$

Properties

Double bonds which are conjugated do not always behave like single ethylenic bonds in chemical reactions; in unconjugated dienes, however, both ethylenic double bonds react independently in the expected manner.

Conjugated systems show characteristic physical properties. Dienes, when conjugated, exhibit absorption bands of greater intensity, and at a lower frequency, than when unconjugated. The absorption bands of hydrocarbons containing short conjugated systems are in the ultra-violet, but as the conjugation increases in length, the absorption moves further into the visible range. Kuhn (3) has shown this to be the case with the terminally phenylated polyenes; as the chain lengthens, the colour passes from yellow to orange, red, blue, and finally black.

The most striking difference, however, between conjugated and unconjugated unsaturated hydrocarbons is in their addition reactions. While in many cases conjugated double bonds add ethylenic reagents in the normal manner by 1,2-addition, many instances are also known where both bonds are involved. Here addition is to the 1- and 4-carbon atoms while the double bond has shifted so that it is between the 2- and 3-carbon atoms.

$$CH_2=CH-CH=CH_2 + X_2 \longrightarrow CH_2X-CH=CH-CH_2X$$

It was this phenomenon of 1,4-addition that Thiele accounted for by his theory of partial valence (7). This theory did not, however, account for the many cases of 1,2-addition which are now known to occur, but which were mostly unknown in Thiele's time. As evidence of 1,2-addition accumulated, his theory had to be abandoned.

No other general theory can be said to have taken its place, although it is now possible to give a fairly satisfactory electronic explanation of most addition reactions. These modern mechanisms of addition have been described by Johnson (8) and others, and will not be dealt with here.

Specific examples of addition reactions to conjugated hydrocarbons will now be considered.

Reduction.

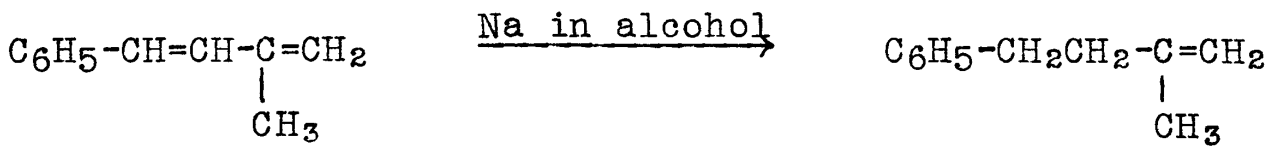
On catalytic reduction these dienes usually take up four atoms of hydrogen to form the corresponding butanes.

Measurements of the reactiion rates seemed to indicate that dihydro compounds were also formed (9,32,137), but careful identification of the reaction products showed that such compounds, if formed at all, were only present in very small amounts (138).

Conjugated diynes of the type $R-C\equiv C-C\equiv C-R$ add hydrogen catalytically by 1,4-addition to give $R-CH=C=C=CH-R$ and $R-CH_2-C\equiv C-CH_2-R$ (10).

Diphenylpolyenes are completely reduced (11) by catalytic methods; one equivalent of hydrogen yields completely reduced product and unchanged polyene.

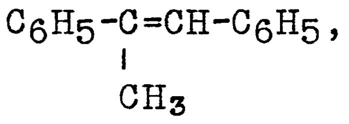
Reduction of dienes or polyenes with sodium or aluminium amalgams, sodium in alcohol or zinc in acetic acid always takes place at the ends of the conjugated system; isolated ethylenic bonds are not further reduced, unless they are in such a position as to be conjugated with the bonds of an aromatic ring. Klages (12) attempted to reduce many dienes and styrenes in this way. He found only one case where there might be a possibility of 1,2-addition to a conjugated system.



$$C_6H_5-CH=CH-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \xrightarrow{\text{Na in alcohol}} C_6H_5-CH_2CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$$

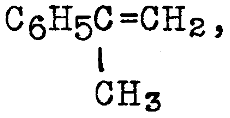
but the nature of the reduced product was uncertain. He found that compounds of the type $ArCH=CH-CH=CH_2$ were reduced to $ArCH_2-CH=CH-CH_3$, and that, in general, the double bonds in compounds of these types,

$C_6H_5CH=CH_2$,

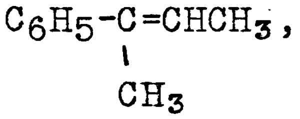


$C_6H_5-C(CH_3)=CH-C_6H_5$,

$C_6H_5CH=CHCH_3$, $(C_6H_5)_2C=CH_2$

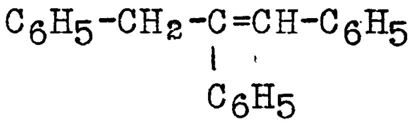


$C_6H_5C(CH_3)=CH_2$,



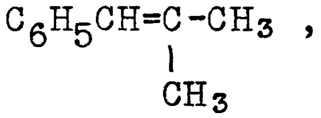
$C_6H_5-C(CH_3)=CHCH_3$,

$C_6H_5CH=CHC_6H_5$,

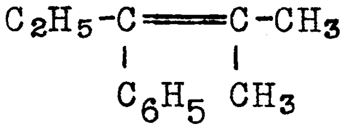


$C_6H_5-CH_2-C(C_6H_5)=CH-C_6H_5$

were reducible by metal combinations. On the other hand, compounds of the type $ArCH_2CH=CHCH_3$ and $ArCH_2CH_2CH=CH_2$ are not reducible by these methods, nor are the following styrenes:

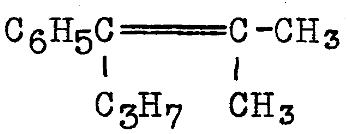


$C_6H_5CH=C(CH_3)-CH_3$,



$C_2H_5-C(C_6H_5)=C(CH_3)-CH_3$

$C_6H_5-CH=C(C_2H_5)_2$,



$C_6H_5C(C_3H_7)=C(CH_3)-CH_3$

Hydration

Dienes are not hydrated directly by treatment with water, but mixtures of acetic acid and sulphuric acid give rise in some cases, (isoprene and 2,3-dimethylbutadiene), to esters of alcohols formed from the dimeric and trimeric hydrocarbons (13,14).

Bromination

In the presence of excess bromine, butadiene forms two stereoisomeric tetrabromides (15,16). If, however, one equivalent of bromine is used, it is found that it, apparently, has added in both the 1,2- and 1,4-positions to give a liquid 1,2-dibromide and a solid 1,4-dibromide. (Griner (17) claimed he obtained two 1,4-dibromides; the solid trans form and a liquid cis-dibromide, but this has not been confirmed). It was found (18,19,20) that if either the 1,2- or solid 1,4-dibromide was heated at 100° an equilibrium mixture was formed which contained 20% 1,2- and 80% 1,4- compound. At -15° 37% of the product was found to be 1,2-dibromide. The yield of 1,4- addition product obtained from the bromination reaction was found to vary with the solvent used. In chloroform at -15°, 63% of the product was 1,4-dibromide; in hexane 38.5% in acetic acid 70%, and in carbon disulphide (at a higher temperature) 65.9%. During bromination there is always an evolution of hydrogen bromide, and hydrogen bromide catalyses the rearrangement of the dibromides. It has been shown (21) that the bromination reaction takes place on a unimolecular layer of the 1,4-dibromide on the walls of the reaction vessel. The 1,2-

dibromide cannot be the primary product since the change to the 1,4-compound is too slow to account for the amount of 1,4-dibromide formed (18).

Isoprene forms a tetrabromide with excess bromine, but, when one equivalent is used, addition is 1,4- (20,22,23). Bromine has also been found to add principally 1,4- to 1,4-dimethylbutadiene, 2,3-dimethylbutadiene (139) and 1,3-dimethylbutadiene (24). However, 1,2- bromination has been found to take place with 1,4-diphenylbutadiene, and with 1-phenylbutadiene to give C_6H_5-CH=CH-CHBrCH$_2$Br (25,26). Ingold (27) reported that 1-bromobutadiene added bromine in the 3,4-positions, but Muskat (28) claimed that 1,4 addition took place.

cis-Hexatriene adds bromine in the 1,2- and trans- in the 1,6- positions (29) but the presence or absence of hydrogen bromide seems to be the deciding factor in this reaction. Butadiynes of the type RC≡C-C≡CR add bromine as they do hydrogen, that is, in the 1,4- positions (10). Cyclohexadiene and cyclopentadiene add bromine in both 1,2- and 1,4- positions, the products are in a mobile equilibrium (18).

Chlorination

Butadiene adds chlorine to give a 1,2- and a 1,4-dichloride; with 2 equivalents of chlorine, the two stereoisomeric tetrachlorides are obtained. The dichlorides, unlike the corresponding dibromides, are stable at 90°. In this case, therefore, the 1,2-dichloride cannot be an intermediate compound which later rearranges to yield the 1,4-dichloride. The 1,4-addition product must be formed directly (30).

Chlorination of 1-phenylbutadiene yields only the 3,4-dichloride under widely differing temperature conditions, and in various solvents. Excess chlorine results in two stereoisomeric tetrachlorides (26).

Iodine Monochloride

Ingold (26,31) added iodine monochloride to ethylenic compounds, which were substituted in such a way that the molecules would be definitely polar. It was found that the iodine atom added predominantly to the negative pole of the molecule. This addition of I^+ was expected to take place before Cl^- added to the other end of the double bond. Ingold then added iodine monochloride to butadiene (32). In methylenechloride at -35° the products were 80% 1,4- and 20% 1,2- addition product; thus in each case the iodine had gone to a terminal carbon atom. This suggests that the first stage of an addition reaction to a conjugated system is co-ordination between I^+ and a negatively polarized terminal carbon atom.

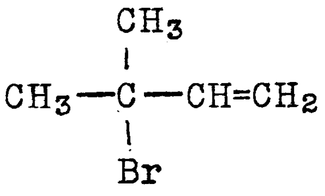
Hydrogen Halides

Butadiene has been reported by several workers (33, 34, 35) to add hydrogen bromide and hydrogen chloride to give 1,4- addition products, but the amount of each formed has been in doubt. Kharasch (36), however, has shown that air or peroxides have a very distinct effect on the mode of addition. In the presence of air or peroxides hydrogen bromide adds mostly 1,4 to butadiene, but in the absence of air and in the presence of antioxidants it adds mostly 1,2 in accordance with Markownikoff's rule. The change from the 1,2- to the 1,4-hydrobromide

$$\underset{\text{XXVI}}{CH_3CH_2Br\text{-}CH=CH_2} \longrightarrow \underset{\text{XXVII}}{CH_3CH=CH\text{-}CH_2Br}$$

is catalysed by hydrogen bromide in the presence of oxygen or peroxides. Kharasch suggests that here 1,4- addition of hydrogen bromide to butadiene at low temperatures is due to a peroxide effect, and that 1,4- addition proceeds by way of 1,2- addition, followed by the catalysed rearrangements.*

The reaction between hydrogen halides and isoprene has been the subject of several investigations, but conflicting results have been reported (37,38,39,40,41). Apparently both 1,4- and 1,2- addition take place; 1,2 addition yielded the tertiary bromide (XXVIII)



$$CH_3\text{—}\overset{\displaystyle CH_3\atop\displaystyle |}{\underset{\displaystyle |\atop\displaystyle Br}{C}}\text{—}CH=CH_2$$

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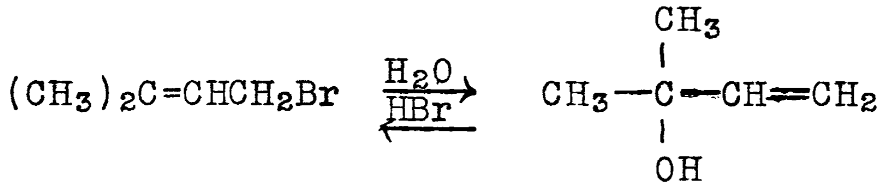
*In a recent paper (148), however, Kharasch states that initial addition of hydrogen halides to butadiene is both 1,2 and 1,4.

which was unstable, changing on standing to the primary 1,4-addition product (XXIX) $(CH_3)_2C{=}CH{-}CH_2Br$ (41). If excess hydrogen bromide was used, the product was found to be the 1,4-hydrobromide. Isoprene and bromine in acetic acid at 0° yielded 74% of 1,4- addition product $(CH_3)_2C{=}CH{-}CH_2Br$ (XXIX) after two days (42). Aqueous hydrochloric acid added to isoprene in the cold to form an unsaturated hydrochloride; the location of the groups has not been determined (43).

The primary 1,4-monohydrobromide (XXIX) is very easily hydrolysed to the tertiary "isoprene alcohol" (XXX) (39). The corresponding primary alcohol cannot be an intermediate, as it has been prepared, and shows no tendency to isomerize under similar experimental conditions (44). This reaction can be reversed by treating the tertiary alcohol with hydrogen bromide.



$$(CH_3)_2C{=}CHCH_2Br \underset{HBr}{\overset{H_2O}{\rightleftarrows}} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH{=}CH_2$$

XXIX XXX

The introduction of negative groups into the butadiene chain has a marked influence on the mode of addition of these halogen hydrides. Thus they add 3,4 to cis- or trans-1-phenylbutadiene[*] to yield $C_6H_5CH{=}CHCHX{-}CH_3$ (45,46).

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[*] These results have not been confirmed, nor have the cis and trans forms of 1-phenylbutadiene been isolated.

Muskat (28) showed that 1-bromobutadiene added hydrogen bromide in the 1,4-positions to give $Br_2CH{-}CH{=}CH{-}CH_3$ and not in the 3,4- as previously reported (27).

Vinylacetylene has been found to add hydrogen halides in the 1,4- positions (47).

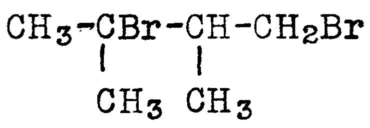
$$CH_2{=}CH{-}C{\equiv}CH + HX \longrightarrow CH_2XCH{=}C{=}CH_2$$

This 2,3-diene changes irreversibly to the conjugated compound, which, in turn, will add hydrogen halide again to the ends of the conjugated system.

$$CH_2XCH{=}C{=}CH_2 \longrightarrow CH_2{=}CXCH{=}CH_2 \longrightarrow CH_3CX{=}CHCH_2X$$

The fact that the change from 2,3- to 1,3- diene is irreversible shows that the primary reaction in this case must be 1,4-addition, and that the apparent 1,2- addition product is only produced by a subsequent rearrangement.

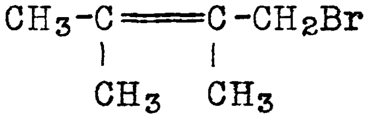
2,3-Dimethylbutadiene (40) adds two molecules of hydrogen bromide to form the 2,4-dibromo-compound,



$$CH_3{-}\underset{CH_3}{\underset{|}{C}}Br{-}\underset{CH_3}{\underset{|}{C}}H{-}CH_2Br$$

as well as about 30 per cent of the 2,3-dibromo-isomer.

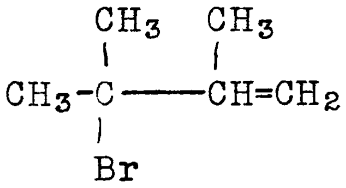
Addition of one molecule of hydrogen halide to 2,3-dimethylbutadiene was considered by Bergmann (40) to yield 30 per cent of 1,4- addition product (XXXI), but the main product was thought to be the 1,2-hydrobromide. Claisen (41), however, found that the main product was the 1,4-addition compound;



$$CH_3\text{-}\underset{CH_3}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}\text{-}CH_2Br$$

XXXI

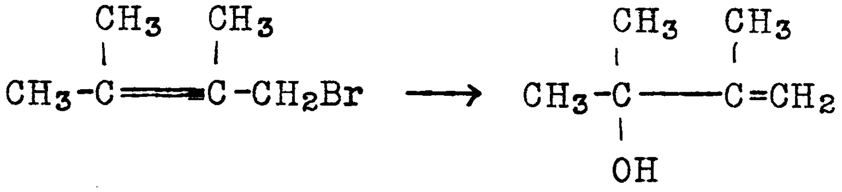
he also found some evidence of the tertiary product



$$CH_3\text{-}\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}\text{—}\overset{CH_3}{\overset{|}{C}}H=CH_2$$

The 1,4-hydrobromide (XXXI) boiled at 51-54° at 20 mm., but, on immediate distillation of the reaction mixture, it was found to boil at 27-50° at 20 mm. This lowering of the boiling point was especially noticeable if there was less than one equivalent of hydrogen bromide present, and was interpreted as indicating primary 1,2-addition of hydrogen bromide to the diene, followed by a slow rearrangement to the 1,4-hydrobromide (XXXI), this rearrangement being catalysed by hydrogen bromide.

Farmer (24) repeated these investigations. He used ozonolysis and permanganate oxidation methods for structure determination, and pointed out that Bergmann's results were doubtful, since he had identified his products by way of the alcohols, without taking into account the fact that such a reaction involves a rearrangement such as was noted with isoprene derivatives. The 1,4-hydrobromide of 2,3-dimethylbutadiene (XXXI) is hydrolysed to a tertiary alcohol by aqueous sodium carbonate.



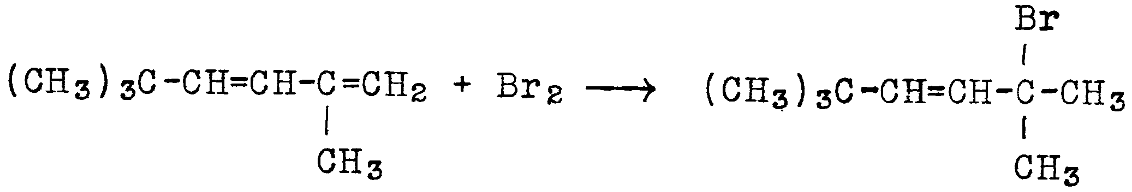
$$CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_2Br \longrightarrow CH_3-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{CH_3}{\overset{|}{C}}=CH_2$$

XXXI

Farmer (48) found that the product of the reaction between 2,3-dimethylbutadiene and hydrogen bromide was almost exclusively the 1,4-hydrobromide (XXXI). He found that the boiling point could be depressed, in the manner observed by Claisen, by adding some diene to the hydrobromide; and concluded that there was no evidence for 1,2-addition taking place first.

1,4-Dimethylbutadiene, on the other hand, yielded 90% 1,2- and 10% 1,4- addition products with hydrogen bromide (48), again with no evidence as to which was the primary product. This may indicate, however, that there is less tendency for a double bond in the middle of the carbon chain to rearrange, than there is for one at a terminal carbon atom.

2,5,5-Trimethyl-1,3-hexadiene adds hydrogen bromide 1,2 to form $(CH_3)_3CCH{=}CH\text{-}C(CH_3)_2Br$ which does not rearrange to a 1,4-product, (71).



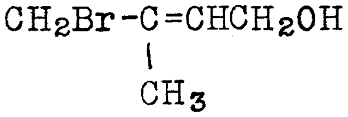
$$(CH_3)_3C\text{-}CH{=}CH\text{-}\underset{\substack{|\\CH_3}}{C}{=}CH_2 + Br_2 \longrightarrow (CH_3)_3C\text{-}CH{=}CH\text{-}\overset{\substack{Br\\|}}{\underset{\substack{|\\CH_3}}{C}}\text{-}CH_3$$

Hypohalous Acids

Halogens, in the presence of water, add to dienes to form halohydrins. Ingold (32) examined these addition reactions in a few cases, his object being to obtain an insight into the mechanism of addition reactions. He considered that Br^+ would first add to a negatively polarized part of the molecule. There would then be a competition between Br^- and OH^- to add to the positively polarized atom. In these cases investigated it was the hydroxyl group which added. By determining the structure of the bromohydrin, the position of attack was found to be the carbon atom occupied by bromine, and this was assumed to be the position of attack in non-aqueous bromination reactions. In such reactions the second bromine atom would be expected to add to the carbon atom corresponding to the one which had previously added the hydroxyl group in the reaction with hypobromous acid. The results Ingold obtained from these reactions were in agreement with those that he had already obtained by adding iodine monochloride to dienes, and pointed to the α- and δ- carbon atoms as the positions of attack.

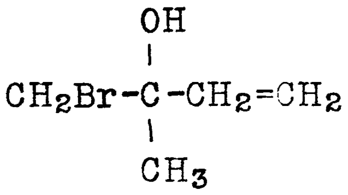
Both mono- and di-halohydrins of dienes may be prepared. Isoprene adds two molecules of hypochlorous acid to form a crystalline dichlorohydrin (49). Cold bromine water yields a mixture of mono-bromohydrins (32).

47%



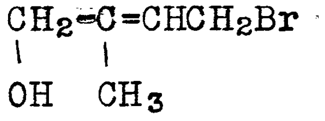
$CH_2Br-\underset{CH_3}{C}=CHCH_2OH$

at least 16%



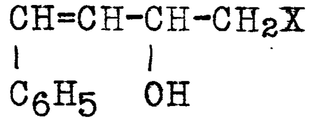
$CH_2Br-\overset{OH}{\underset{CH_3}{C}}-CH_2=CH_2$

and in small quantities,



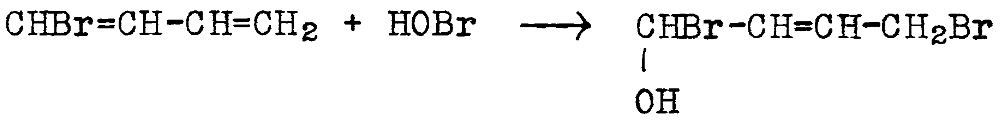
$\underset{OH}{CH_2}-\underset{CH_3}{C}=CHCH_2Br$

Muskat and Grimsley (50) reported that hypohalous acids gave 3,4- addition with 1-phenylbutadiene, yielding



$$\underset{C_6H_5}{CH}=CH-\underset{OH}{CH}-CH_2X$$

These compounds are unstable, and can be converted, by treatment with potassium hydroxide, into the corresponding ethylene oxides. Abragam and Deux (51) claim, however, that the ethylene oxide obtained is that corresponding to one or both of the two possible 1,2-chlorhydrins of 1-phenylbutadiene. Muskat (28) also found that hypobromous acid added in the 1,4- positions to 1-bromobutadiene.



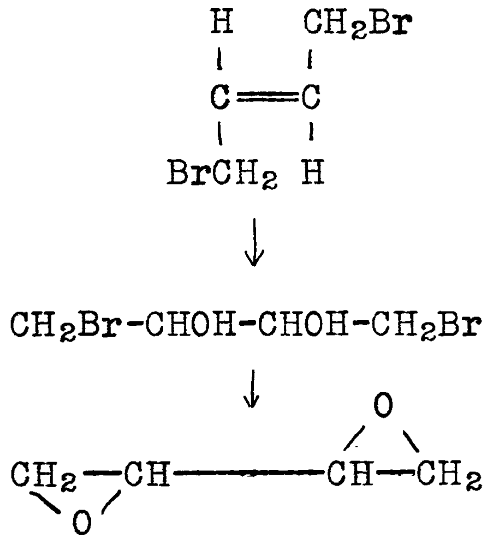
$$CHBr=CH-CH=CH_2 + HOBr \longrightarrow \underset{OH}{CHBr}-CH=CH-CH_2Br$$

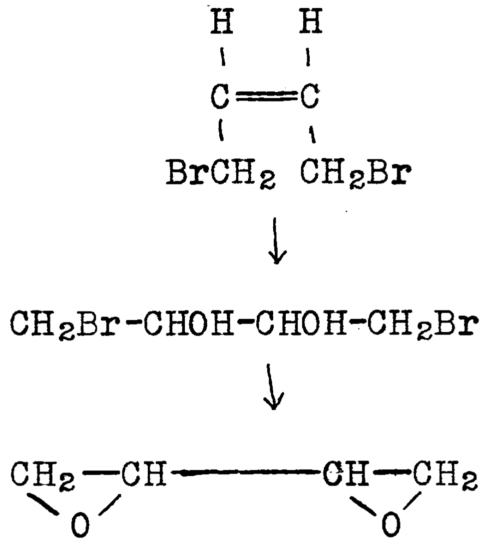
Muskat (140) reported that hypohalous acids added 1,2 to vinylacrylic acid to form a δ-hydroxy acid.

$$CH_2=CH.CH=CH.COOH \longrightarrow CH_2OH.CHCl.CH=CH.COOH$$

Farmer, however, showed that this was incorrect and that the chlorine went to the δ-carbon atom (141). This invalidated the theoretical arguments on which Muskat's work was based (30).

Griner (17) treated the two geometrically isomeric dibromides of butadiene with permanganate, and obtained two stereoisomeric dibromhydrins, which were converted into two stereoisomeric oxides by caustic alkali.





Phosphorus Pentachloride.

Phosphorus pentachloride adds to the terminally unsubstituted double bond of 1-phenylbutadiene.

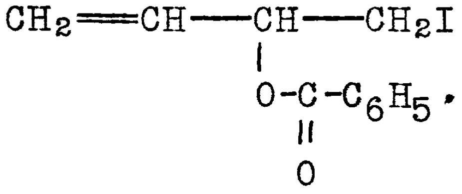
$$C_6H_5CH{=}CH{-}CH{=}CH_2 + PCl_5 \longrightarrow C_6H_5CH{=}CH{-}CHClCH_2PCl_4$$

$$\xrightarrow{H_2O} C_6H_5{=}CHCH{=}CHPO_3H_2$$

1,4-Diphenylbutadiene and 1-phenyl-4-methylbutadiene do not react with phosphorus pentachloride.

Iodo-silver benzoate.

Prévost (53) found that iodosilver benzoate, $(C_6H_5COO)_2AgI$, with excess butadiene seems to add mainly in the 1,2- positions giving



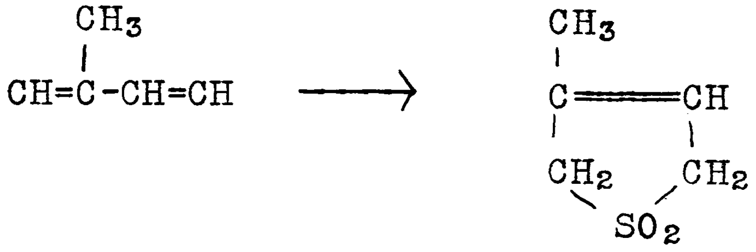
$$CH_2{=}CH{-}\underset{\underset{\overset{\|}{O}}{O-C-C_6H_5}}{CH}{-}CH_2I.$$

Sulphur compounds.

While sulphur dioxide is most often used to produce resinous polymers from dienes - especially from butadiene, piperylene, isoprene and 2,3-dimethylbutadiene, - monomeric crystalline sulphones have also been obtained in many cases (54). Both polymer and monomer may be formed simultaneously, but the monomeric sulphones cannot be transformed into the polymers, and are not, therefore, intermediates. Anti-oxidants increase the yield of the monomeric sulphones (55). The following butadiene derivatives have been found by Backer (56) to yield crystalline sulphones:

1,2,3,4-tetramethylbutadiene,
1,4-dimethylbutadiene,
2,3-diethylbutadiene,
2-t-butylbutadiene,
2,3-di-t-butylbutadiene,
2-phenylbutadiene,
2,3-diphenylbutadiene.

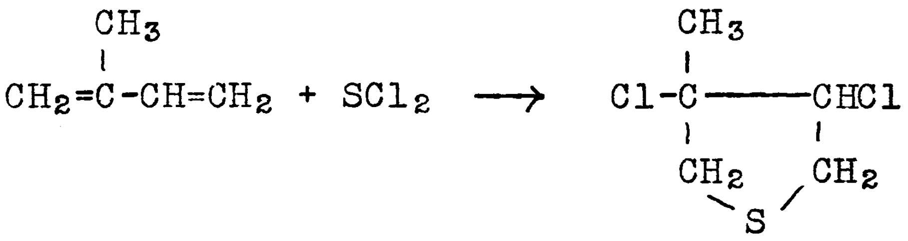
He also found (57) that many of these dienes yielded selenones with SeO_2. The structures of these compounds have been determined and they are found to be thiophene derivatives (or the selenium analogues).

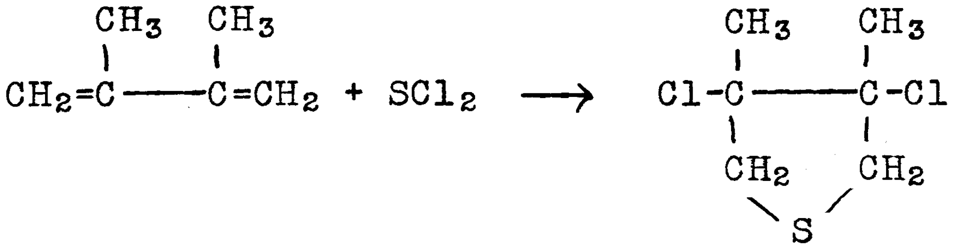


These sulphones can be decomposed by heat to regenerate the dienes, and in some cases this is a useful method of purification. The addition of SO_2 is always conjugate.

The SO_2 can be added directly as a liquid, or in ether solution at 100°. It can also be made to add in the form of sulphurous acid or ammonium bisulphite (58).

Certain dienes will react with sulphur dichloride to form reduced thiophene derivatives (59).



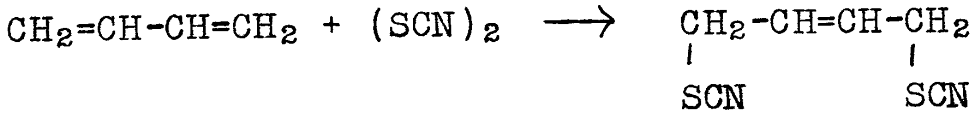


In the case of butadiene however, chlorination takes place.

$$CH_2=CH-CH=CH_2 + SCl_2 \longrightarrow CH_2Cl-CHCl-CHCl-CH_2Cl$$

When butadiene is treated with hydrogen sulphide at 600° in the presence of a pyrite catalyst it reacts to form thiophene in yields of 30-60% (60). Thiophene derivatives have also been prepared by pouring dienes, such as butadiene, isoprene, 2,3-dimethylbutadiene and 3,4-dimethylbutadiene, onto molten sulphur (61).

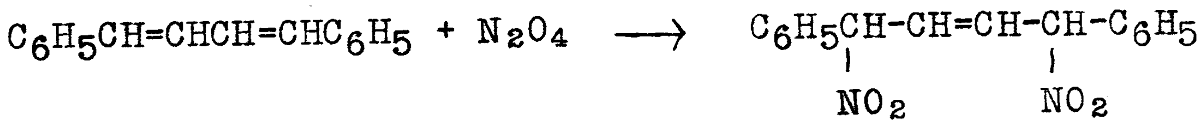
Bruson (62) reported that thiocyanogen added to isoprene and 2,3-dimethylbutadiene to form crystalline dithiocyano-compounds. Müller (63) has since shown that butadiene gives 1,4-dithiocyanobutene in 80% yield. This would be expected, as thiocyanogen adds to ethylenic bonds in much the same way as do the halogens.



$$CH_2=CH-CH=CH_2 + (SCN)_2 \longrightarrow \underset{SCN}{CH_2}-CH=CH-\underset{SCN}{CH_2}$$

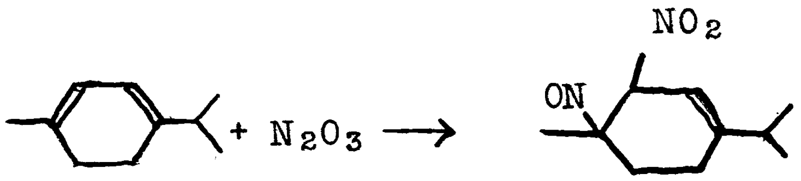
Nitrogen Compounds.

Oxides of nitrogen add to 1,4-diphenylbutadiene in the 1,4- positions (64,142).

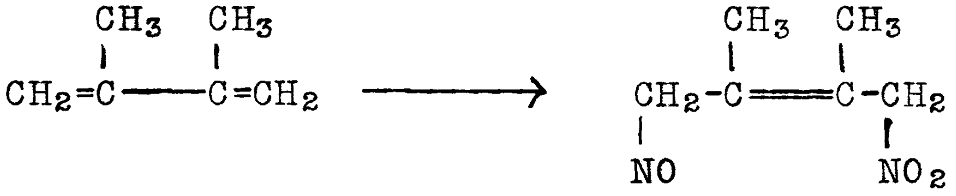


$$C_6H_5CH=CHCH=CHC_6H_5 + N_2O_4 \longrightarrow C_6H_5\underset{NO_2}{CH}-CH=CH-\underset{NO_2}{CH}-C_6H_5$$

Nitrogen trioxide has been found (65) to add 1,2 to terpinene.

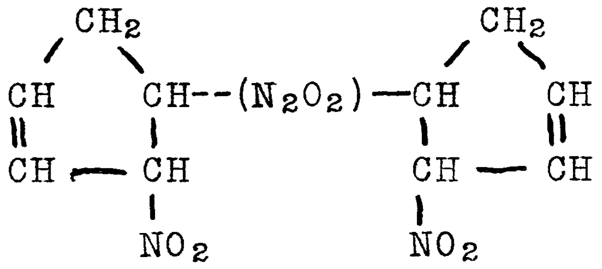


In the case of 2,3-dimethylbutadiene however, 1,4-addition has been found to take place (66).



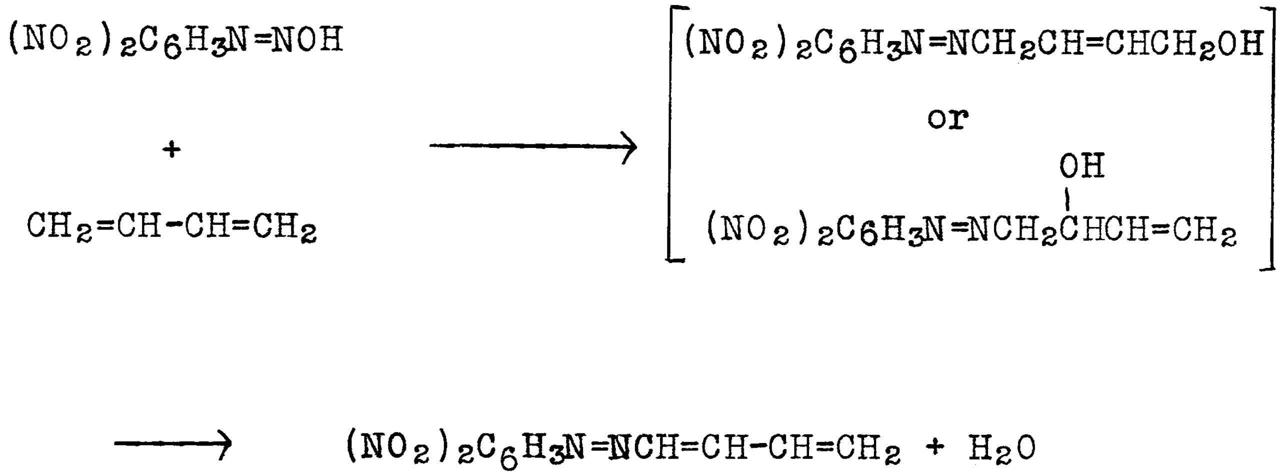
$$\mathrm{CH_2{=}}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}{-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{{=}CH_2} \longrightarrow \underset{\underset{\mathrm{NO}}{|}}{\mathrm{CH_2}}{-}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}{=}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}{-}\underset{\underset{\mathrm{NO_2}}{|}}{\mathrm{CH_2}}$$

Wieland believed that nitrogen trioxide added to cyclopentadiene to form bimolecular compound (142).



1,3-Cyclohexadiene has recently been shown to add nitrogen trioxide in the 1,4-positions (143).

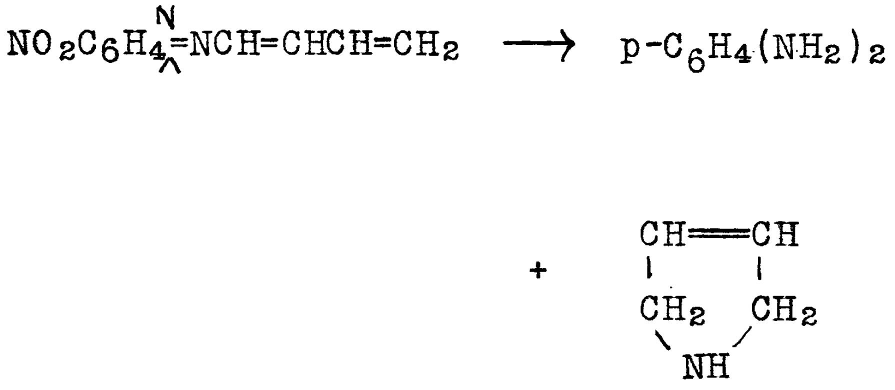
Meyer (67) found that diazonium salts of p-nitroaniline and 2,4-dinitroaniline coupled with butadiene, isoprene, piperylene and 2,3-dimethylbutadiene in acetic acid or alcohol to give colored crystalline azo compounds.



$$\begin{array}{c}\mathrm{(NO_2)_2C_6H_3N{=}NOH}\\ +\\ \mathrm{CH_2{=}CH{-}CH{=}CH_2}\end{array} \longrightarrow \left[\begin{array}{c}\mathrm{(NO_2)_2C_6H_3N{=}NCH_2CH{=}CHCH_2OH}\\ \text{or}\\ \mathrm{(NO_2)_2C_6H_3N{=}NCH_2\overset{\overset{OH}{|}}{C}HCH{=}CH_2}\end{array}\right]$$

$$\longrightarrow \mathrm{(NO_2)_2C_6H_3N{=}NCH{=}CH{-}CH{=}CH_2 + H_2O}$$

Terentiev (68) and Fieser (69) have used this reaction as a qualitative colour test for conjugated compounds. Those dienes tested included butadiene, 1-methylbutadiene, 2,3-dimethylbutadiene, 1,4-dimethylbutadiene, 1,1,4,4-tetramethylbutadiene, and 1,4-diphenylbutadiene. Terentiev used diazotized p-nitroaniline, 2,4-dinitroaniline and p-phenylenediamine in phosphoric acid, while Fieser used diazotized p-nitroaniline in acetic acid and in dioxane-acetic acid mixtures. Arbuzov (70) has pointed out that some dinitrodiazoaminobenzene is always formed, making the method unreliable. He treated the product obtained by coupling butadiene to diazotized p-nitroaniline, with stannous chloride in hydrochloric acid and obtained p-phenylenediamine and pyrroline.

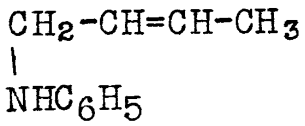


$$NO_2C_6H_4\overset{N}{\wedge}{=}NCH{=}CHCH{=}CH_2 \longrightarrow p\text{-}C_6H_4(NH_2)_2$$

Conjugated dienes have been reported (72) to add ammonia and amines in the presence of an alkali metal, alumina, magnesia or barium chloride, to form unsaturated organic bases - probably butenylamines.

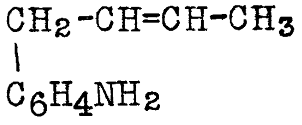
Butadiene and ammonia at 550°, in the presence of a catalyst made from cadmium and aluminium nitrates on silica gel, yield 4% pyrrole (60).

Aniline hydrochloride was found to add to butadiene, giving complex amines, among which were



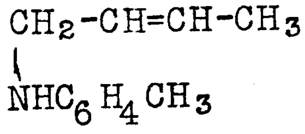
$$\underset{NHC_6H_5}{\underset{|}{CH_2}}\text{-}CH{=}CH\text{-}CH_3$$

and



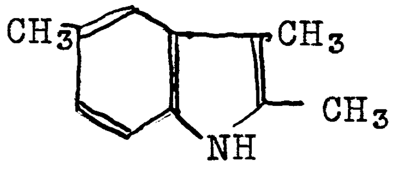
$$\underset{C_6H_4NH_2}{\underset{|}{CH_2}}\text{-}CH{=}CH\text{-}CH_3$$

p-Toluidine gave



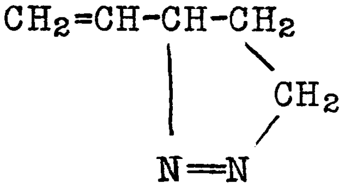
$$\underset{NHC_6H_4CH_3}{\underset{|}{CH_2}}\text{-}CH{=}CH\text{-}CH_3$$

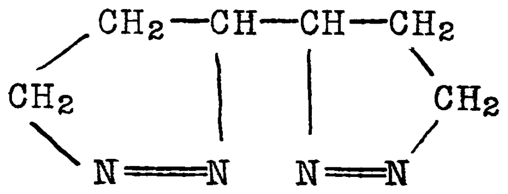
and



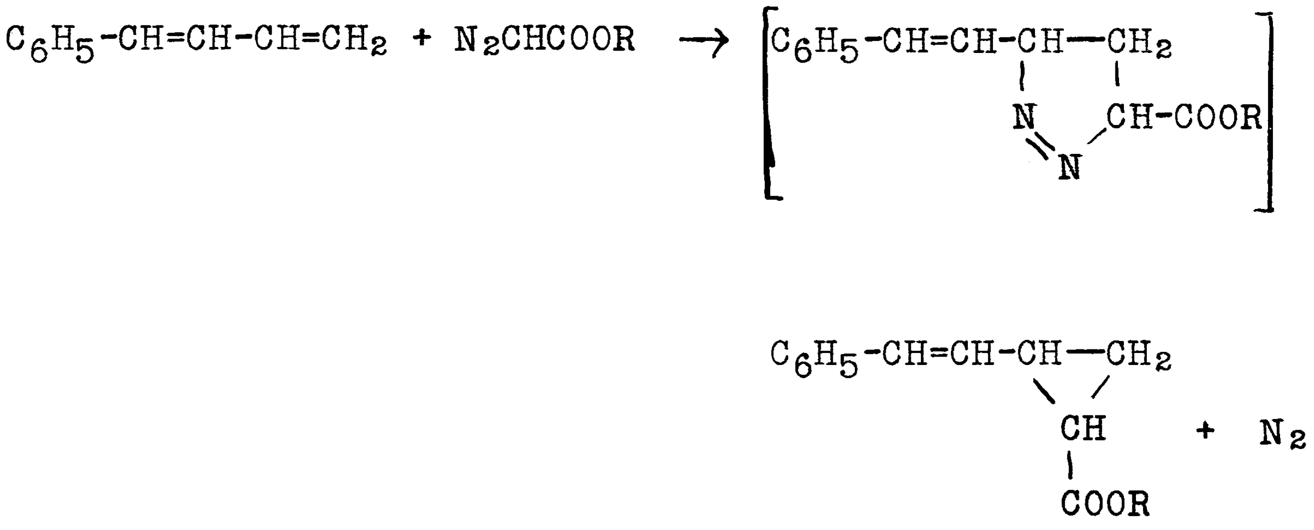
as well as other butenylamines (73).

Butadiene will add one or two moles of diazomethane to give 5-vinylpyrazoline and 5,5'-dipyrazoline (74).



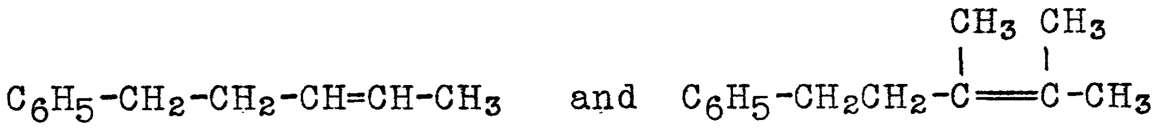


This means that two 5-membered rings have been formed by 1,2-addition, rather than a 7-membered ring by 1,4-addition. Diazoacetic ester adds in a similar manner to 1-phenylbutadiene (144).



Hydrocarbons.

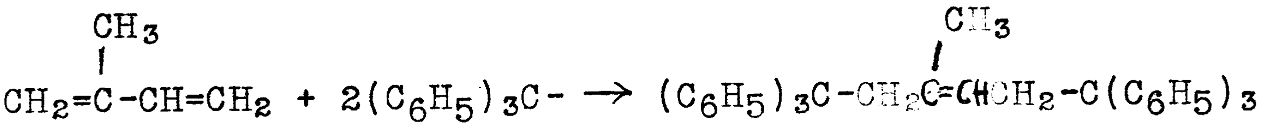
It has been claimed that toluene will add to butadiene and 2,3-dimethylbutadiene, in the presence of sodium in an autoclave at 160°, to give 1,4-addition products (75).



$$C_6H_5\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH\text{-}CH_3 \quad \text{and} \quad C_6H_5\text{-}CH_2CH_2\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=\!=}\overset{\displaystyle CH_3}{\overset{|}{C}}\text{-}CH_3$$

Unsaturated hydrocarbons such as amylene, pinene, trimethylethylene, isopinene, dipentene and sylvestrene condense with isoprene, in the presence of aluminium chloride, to form compounds which are usually resinous in nature (106).

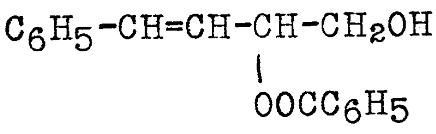
Two moles of triphenylmethyl add 1,4 to isoprene and 2,3-dimethylbutadiene (76).



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}\text{-}CH{=}CH_2 + 2(C_6H_5)_3C\text{-} \rightarrow (C_6H_5)_3C\text{-}CH_2\overset{\displaystyle CH_3}{\overset{/}{C}}{=}CHCH_2\text{-}C(C_6H_5)_3$$

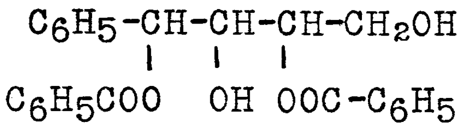
Other Addition Reactions.

cis-1-Phenylbutadiene reacts with perbenzoic acid in chloroform at 0° to form what is probably the 1,2- addition product.



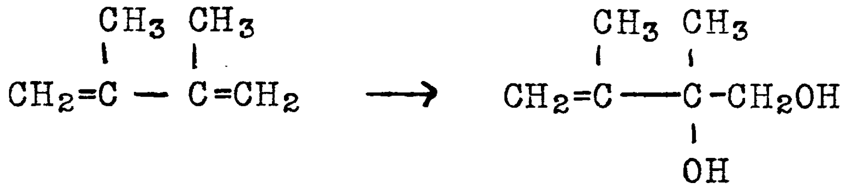
$$C_6H_5\text{-}CH{=}CH\text{-}\underset{\displaystyle OOCC_6H_5}{\underset{|}{CH}}\text{-}CH_2OH$$

At 25° two mols of perbenzoic acid are added (77).



$$\begin{array}{l} C_6H_5\text{-}\underset{\underset{\displaystyle C_6H_5COO}{|}}{CH}\text{-}\underset{\underset{\displaystyle OH}{|}}{CH}\text{-}\underset{\underset{\displaystyle OOC\text{-}C_6H_5}{|}}{CH}\text{-}CH_2OH \end{array}$$

2,3-Dimethylbutadiene can be oxidized in the 1,2- positions to the 1,2-diol by lead tetracetate (78).



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2 \longrightarrow CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\text{-}CH_2OH$$

1,4-Dimethylbutadiene yields the diacetate of a hexenediol.

Mercuric acetate in methyl alcohol (79) adds the elements of methoxymercuric acetate to 1-phenylbutadiene. The addend first formed is probably a 3,4- addition product.

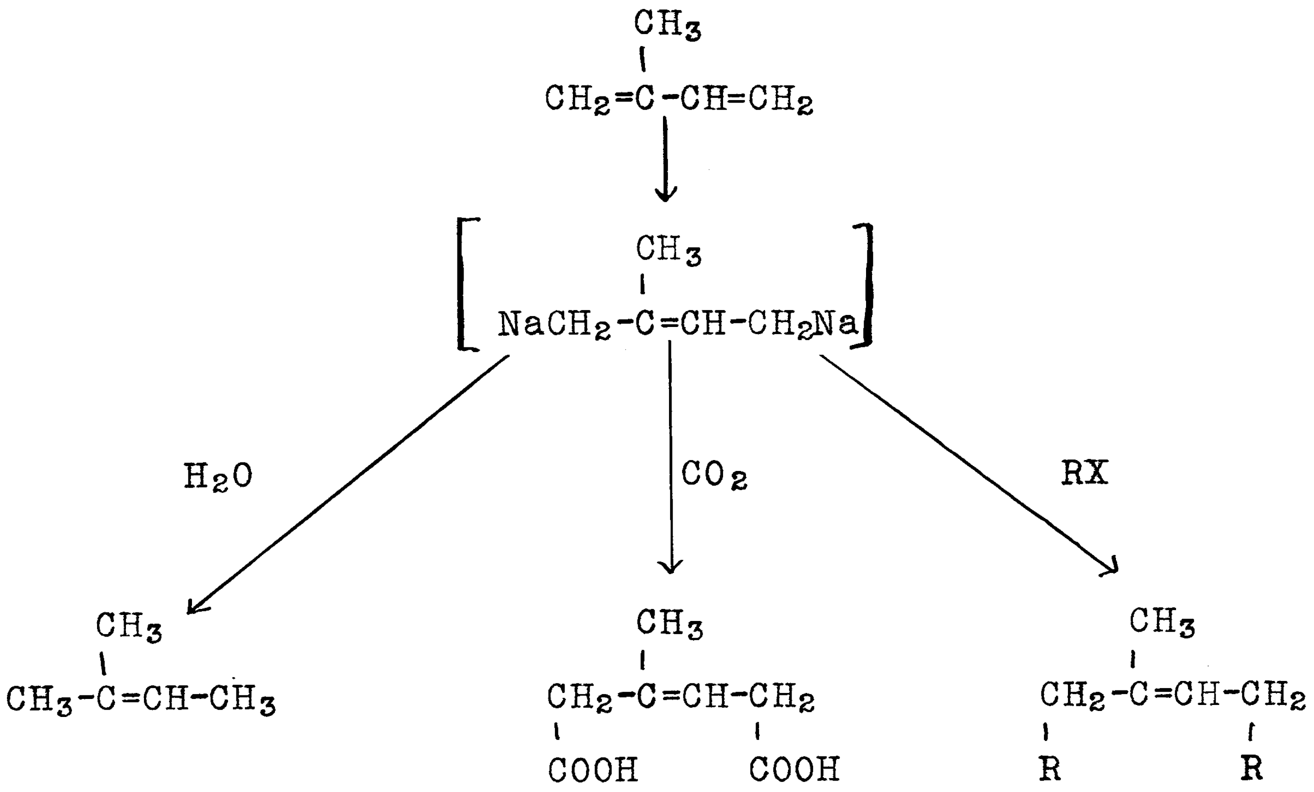
Diphenylketene has been reported (80) to add to piperylene and 2,3-dimethylbutadiene, The crystalline addition compounds seem to contain four-carbon rings.

Dienes have been shown to form molecular compounds with ferric chloride and antimony trichloride (81), with iron carbonyl (92), and with cuprous chloride (93). Kuhn (84) found that his polyenes, including 1,4-diphenylbutadiene, formed coloured molecular compounds when melted with the following substances: quinone, maleic anhydride, phthalic anhydride, tetrachlorophthalic acid, oxalyl chloride, fumaryl chloride, phthalyl chloride, thionyl chloride, sulphuryl chloride, 1,3,5-trinitrobenzene, picric acid and styphnic acid.

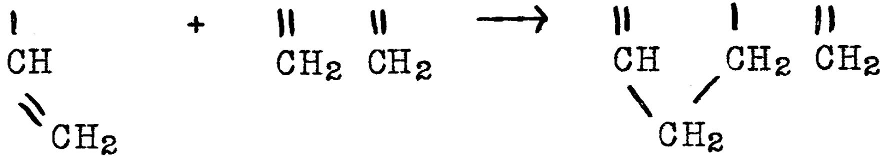
Polymerization

This subject is too extensive to be covered here; it may be mentioned, however, that conjugated butadienes tend to polymerize very easily, forming either cyclic dimerides, or rubber-like polymers of high molecular weight. Polymerization can be induced by a very large number of reagents and catalysts. In the air, many of the dienes slowly change to gums and tars. This change is believed to be brought about by the addition of oxygen to form gum-like peroxides (85). Monozonides are easily obtained from these dienes, but diozonides are only formed slowly.

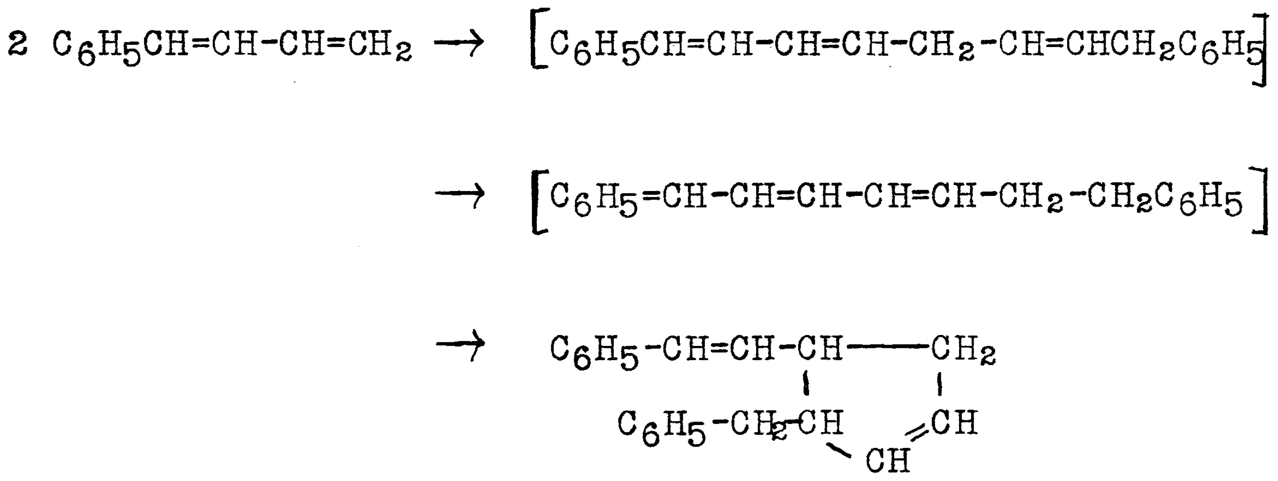
Ziegler (86) has shown that alkali metals add to dienes, apparently both 1,2 and 1,4. He considers that such addition is the slow first step in the polymerization reactions which these compounds undergo in the presence of alkali metals. The alkali-organic addition products add to the dienes with extraordinary rapidity. Midgley also studied polymerization of isoprene by alkali metals (87); he succeeded in adding sodium to isoprene in liquid ammonia. The 60% yield of 2-methyl-2-butene obtained on adding water indicated that the sodium had added 1,4. In the presence of alkvlhalides and carbon dioxide such compounds are alkylated and carboxylated respectively (88).



Some of the oily products of polymerization are found to be cyclic dimers, probably formed by a Diels-Alder reaction between two diene molecules (145).



All the cyclic dimers are cyclohexene derivatives of this type (141). In the case of unsymmetrical dienes there is a possibility of structural isomerism in the products (89). Bergmann (90) has shown that 1-phenylbutadiene can dimerize to form a cyclopentadiene derivative (141).



$$2\ C_6H_5CH{=}CH{-}CH{=}CH_2 \rightarrow [C_6H_5CH{=}CH{-}CH{=}CH{-}CH_2{-}CH{=}CHCH_2C_6H_5]$$

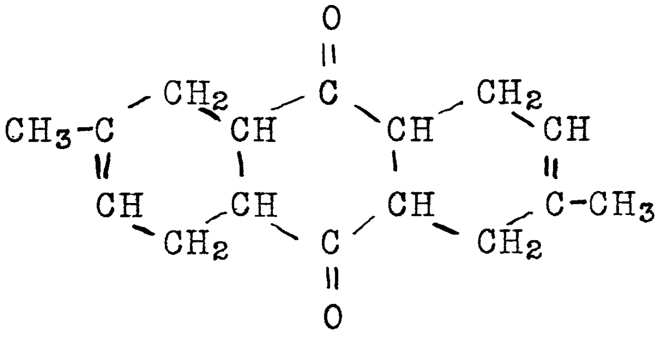
$$\rightarrow [C_6H_5{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}CH_2C_6H_5]$$

$$\rightarrow \begin{array}{l} C_6H_5{-}CH{=}CH{-}CH{-}{-}{-}CH_2 \\ C_6H_5{-}C\cancel{H_2}{-}CH \quad CH{=}CH \end{array}$$

While dimers and polymers are obtained together, the dimers alone cannot be made to form the rubber-like polymers. This indicates that the first step in the formation of these polymers cannot be the formation of cyclic dimers. The yields of polymers are very sensitive to reaction conditions, and vary greatly with the diene used. It has been found (91) that dienes with methyl substituents on the end of the chain have less ~~a greater~~ tendency to polymerize than those with methyl groups on the central carbon atoms. Phenyl substitution, as far as 1,4- and 2,3-diphenylbutadienes are concerned, seems to have just the same ~~reverse~~ effect.

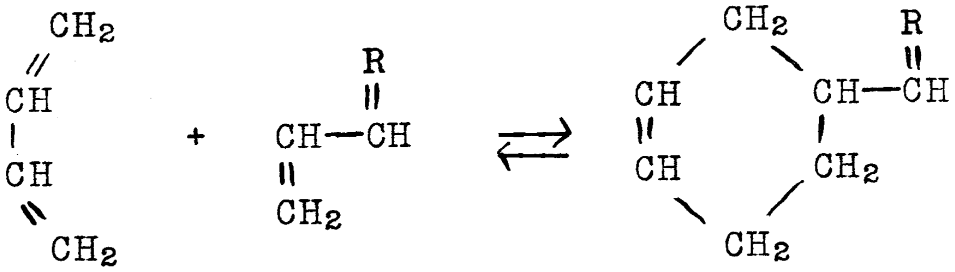
The Diene Synthesis.

The diene synthesis is the most characteristic reaction of conjugated dienes. Von Euler and Josephson in 1920 (92) found that isoprene could be condensed with benzoquinone to yield a white crystalline solid. To this they assigned the provisional formula

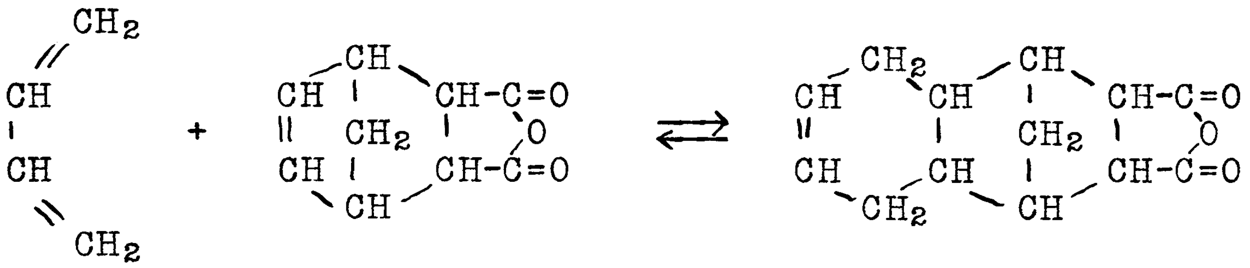


since it could be brominated to form a tetrabromide, and would form a dioxime.

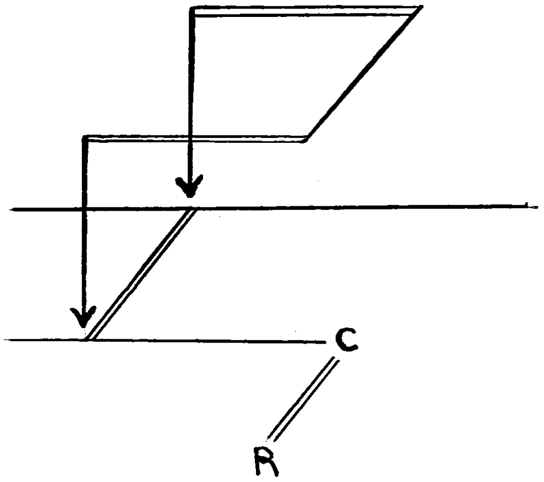
Diels and Alder in 1928 (93) reported a comprehensive investigation of this reaction, in which they had succeeded in adding many active ethylenic compounds to a wide variety of dienes. The reaction always involved 1,4- addition of active ethylenic compounds to the diene to form cyclic compounds.



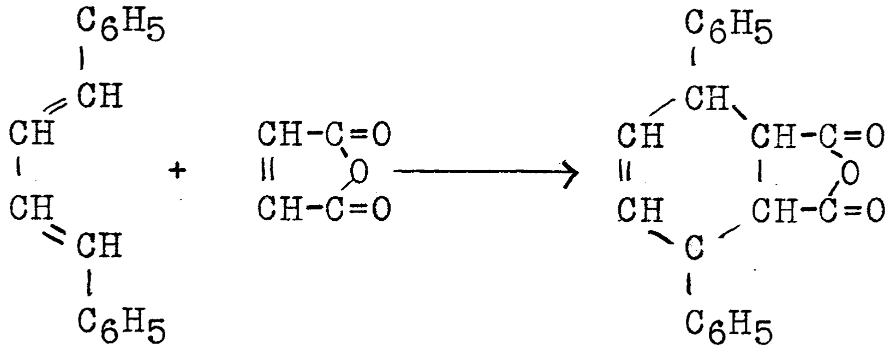
The activation of an ethylenic or acetylenic bond can result from the presence of an unsaturated group which is α, β with respect to the double or triple bond. These activating groups may be C=O, CN, C=C or, probably, NO_2 (95). Certain bridged compounds, already formed by the diene syntheses, possess such active ethylenic linkages, although here the activation must be due to steric effects (96).



Alder (94) has shown that the diene adds to the active ethylenic linkage in the cis- position.



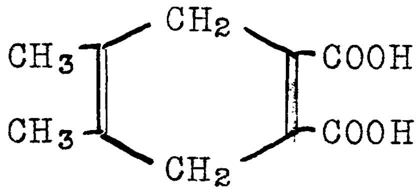
The addition of maleic anhydride to dienes leads to the formation of tetrahydrophthalic anhydrides, which are often useful derivatives for purposes of identification.



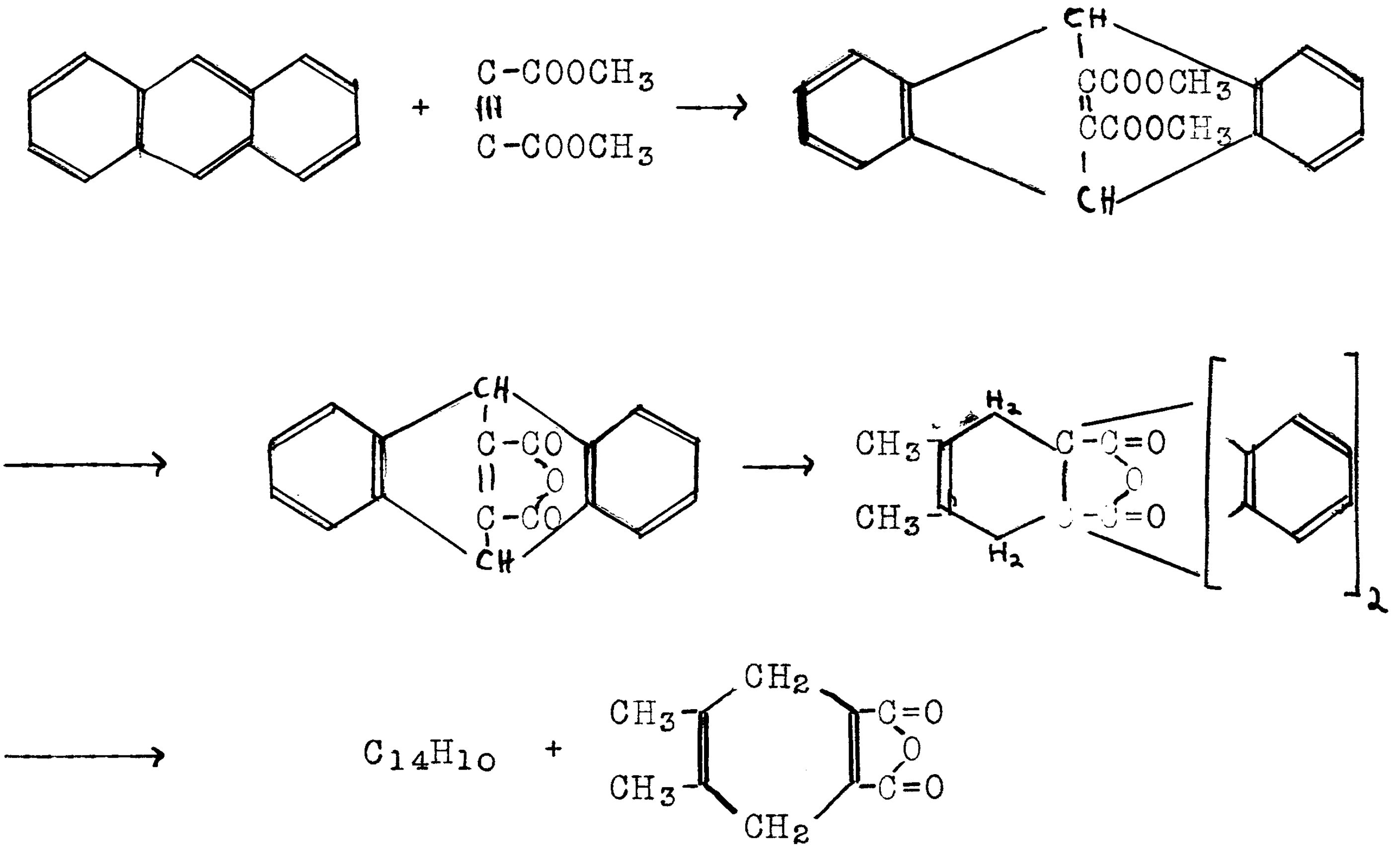
These anhydrides, or the sodium salts of the acids, can be catalytically reduced to the cyclohexane dicarboxylic acids (93), or oxidized by permanganate to butane-1,2,3,4-tetracarboxylic acids (97). Dehydrogenation with nitric acid gives the corresponding phthalic acid (98). When 1-phenylbutadiene or 1,4-diphenylbutadiene reacts with maleic anhydride, the products may be degraded to diphenyl or terphenyl respectively by distilling the calcium salt of the acids with lime and zinc dust (99). Potassium ferricyanide in alkaline solution has also been used to dehydrogenate and decarboxylate these acids to the corresponding aromatic hydrocarbons (100).

Many quinones have been found to add to dienes. Benzoquinone can add one or two molecules of a diene. The resulting compounds are easily dehydrogenated in alkaline solution by the oxygen of the air to yield naphthoquinone and anthraquinone derivatives.

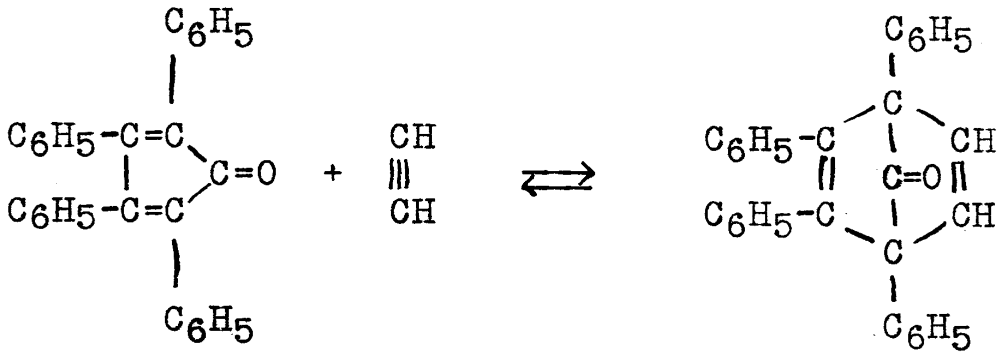
Acetylenedicarboxylic ester is another compound which is frequently used in the diene synthesis. Diels (101) added the dimethyl ester of acetylene dicarboxylic acid to 2,3-dimethylbutadiene and obtained, on hydrolysis, a dihydrophthalic acid.



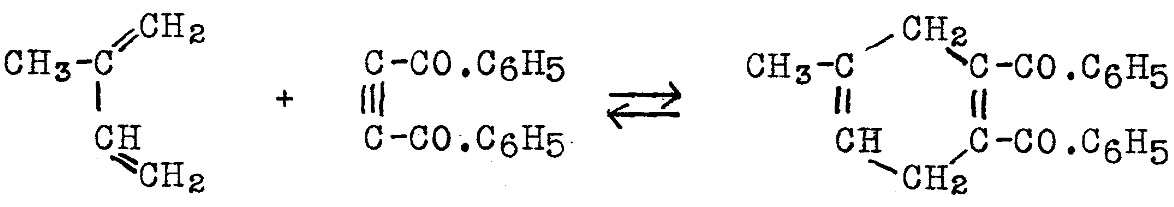
A geometrical isomer of this acid was formed by adding the diene to the anhydride prepared from a diene synthesis between anthracene and the acetylenic ester, and distilling.



Dilthey (102) has added a number of substances, some of which might not be considered as having very active ethylenic linkages, to active dienes, like tetraphenylcyclopentadienone. These include acetylene, phenylacetylene, phenyl propiolic acid ethyl ester, the acetal of phenyl propionaldehyde, diphenylacetylene, benzonitrile and diphenylethylene.

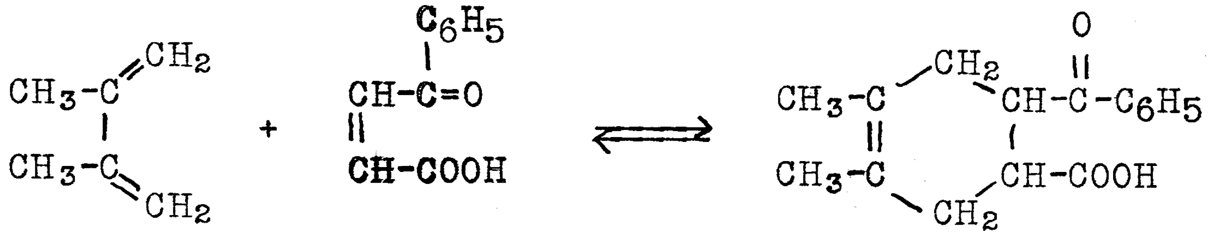


Isoprene and 2,3-dimethylbutadiene react in a similar manner with dibenzoylacetylene (32).

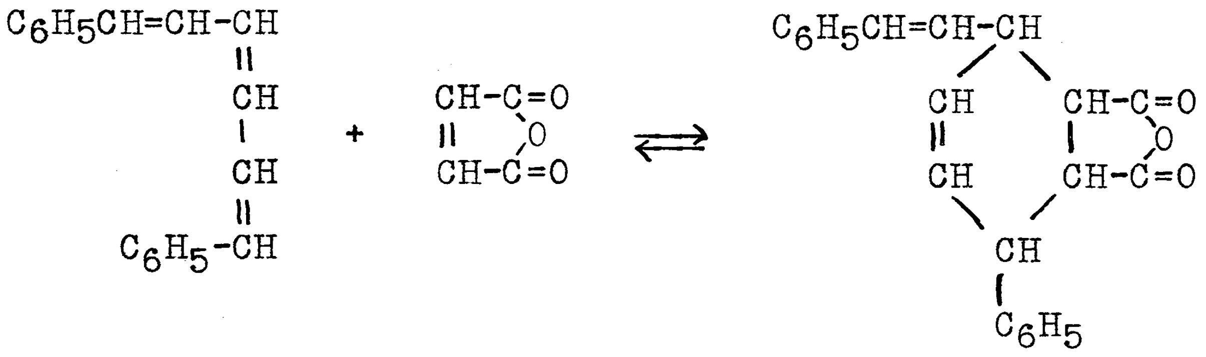


These compounds lose carbon monoxide on heating, and are easily dehydrogenated to aromatic substances (103).

Aroyl acrylic acids add to some dienes, subsequent dehydrogenation and ring-closure yield anthraquinones (104).

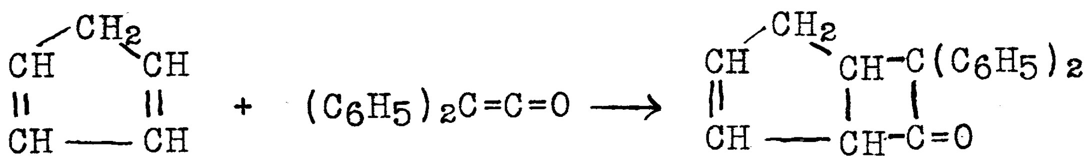


Polyenes add one mole of maleic anhydride for each pair of conjugated double bonds in the chain (100). Addition even in the case of hexatrienes, is always 1,4.

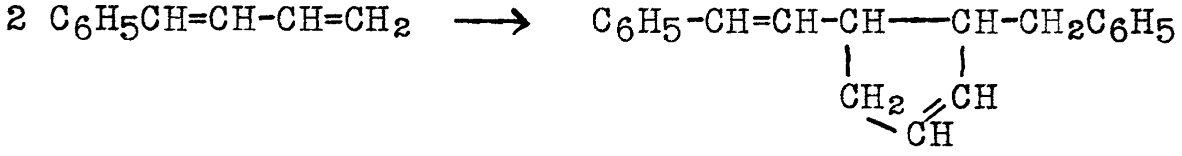


The diene synthesis is a reversible reaction, and maximum yields are only obtained under the proper conditions of concentration, temperature and time (105). Except in industrial applications, catalysts have seldom been used.

Two exceptions to the generality of the diene synthesis may be mentioned. Diphenylketene adds 1,2 to cyclopentadiene (146),



and 1-phenylbutadiene has been shown to dimerize in the following manner, (90).



Phenylbutadienes

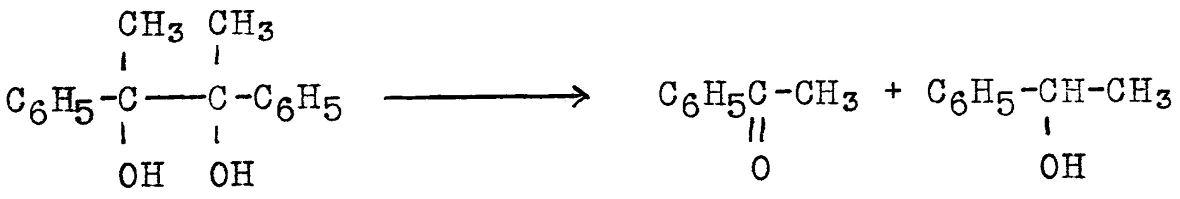
It can be seen, from the reactions already considered, that phenyl groups do not have any very marked effect on the properties of the dienes. Phenyl groups are considered to be "negative groups", and will tend to repel electrons. These groups greatly increase the conjugation of the system, and Fieser (107) has shown that such phenylated conjugated systems closely resemble aromatic systems in many respects. He points out that no one has succeeded in adding hydrogen bromide to 1,4-diphenylbutadiene, and that, during catalytic hydrogenation of the α,ω-diphenylpolyenes, the intermediate reduction products, like those of benzene, seem to be more rapidly reduced than the starting material.

2-Phenylbutadiene, and 2,3-diphenylbutadiene seem to be the only conjugated hydrocarbons which have been made whose phenyl groups are not attached to one or both of the end carbon atoms. Compounds of this type would be expected to resemble the styrenes. The terminal hydrogen atoms would be activated to some extent by the phenyl groups; coupling and polymerization would probably be easy. On the other hand, when 1,4- addition had taken place, the resulting 2,3- double bond would be expected to be rather inactive, as in the extreme case of tetraphenylethylene, where bromine does not add to the ethylenic bond, but enters the phenyl groups (108).

$$(C_6H_5)_2C=C(C_6H_5)_2 + 4Br_2 \longrightarrow (C_6H_4Br)_2C=C(C_6H_4Br)_2 + 4HBr$$

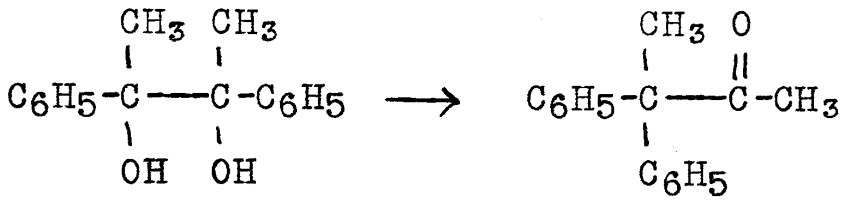
2,3-Diphenylbutadiene

2,3-Diphenylbutadiene was first prepared in 1880 by Thörner and Zincke (109). These investigators were studying the properties of pinacols and pinacolones. They found that, while acetophenonepinacol was cleaved by heat alone,



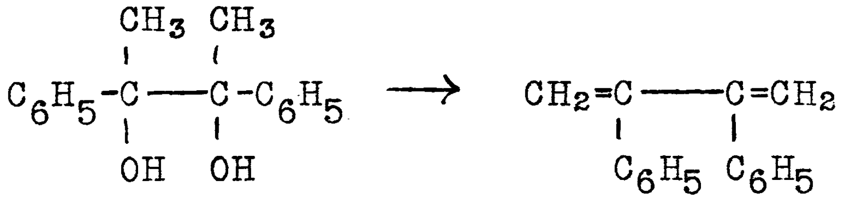
$$C_6H_5-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-C_6H_5 \longrightarrow C_6H_5\underset{\overset{\|}{O}}{C}-CH_3 + C_6H_5-\underset{OH}{CH}-CH_3$$

and underwent rearrangement by the action of acids or alkalis,



$$C_6H_5-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-C_6H_5 \longrightarrow C_6H_5-\underset{C_6H_5}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

heating the pinacol with acetic anhydride in a sealed tube at 180-200°, produced a hydrocarbon, $C_{16}H_{14}$. This differs from the behaviour of benzo- and tolylphenonepinacols with acetic anhydride, which were found to be unaltered at moderate temperatures, and split to the corresponding ketones and alcohols at high temperatures. Apparently acetophenonepinacol was dehydrated under these conditions.



$$\underset{\text{IV}}{C_6H_5-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-C_6H_5} \longrightarrow \underset{\text{V}}{CH_2=\underset{C_6H_5}{C}-\underset{C_6H_5}{C}=CH_2}$$

IV V

The hydrocarbon was obtained as an oily liquid, and was accompanied by a large quantity of resin, from which it was separated by steam distillation. After standing a long time, the oil solidified, and was then crystallized from alcohol into long, colourless prisms melting at 49-49.5°. Analytical values for carbon were low; calculated, C, 93.2; H, 6.8%; found C, 90.96; H, 7.08%. Further attempts at purification of the diene were useless however, as it rapidly polymerized into a resinous mass, apparently under the influence of light.

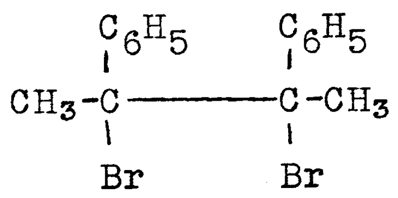
Beschke prepared what was apparently 2,3-diphenylbutadiene in 1912 (see below).

No more work was done on this compound until 1917, when Johlin repeated Thörner and Zincke's work (110). He heated acetophenonepinacol with excess acetic anhydride in a sealed tube for three hours at 180°. The reaction mixture was diluted with water, neutralized with sodium carbonate, and steam distilled. The hydrocarbon was carried over and readily crystallized. It was easily recrystallized from alcohol, and melted at 49°.

Johlin mentioned however, that this sealed tube reaction gave varying results. He stated that a brown liquid was generally the reaction product, but that in one instance a viscous, somewhat elastic, ribbon was formed in the glass tube. This material was insoluble in many of the solvents which will dissolve 2,3-diphenylbutadiene; such as ether, acetone and petroleum ether. It was quite soluble in benzene and chloroform. It could not be prepared a second time, and Johlin considered that it was probably a product of polymerization of the diene. He also mentioned that the diene spontaneously changed into a resinous material. He considered that there was no doubt as to the identity of this diene with

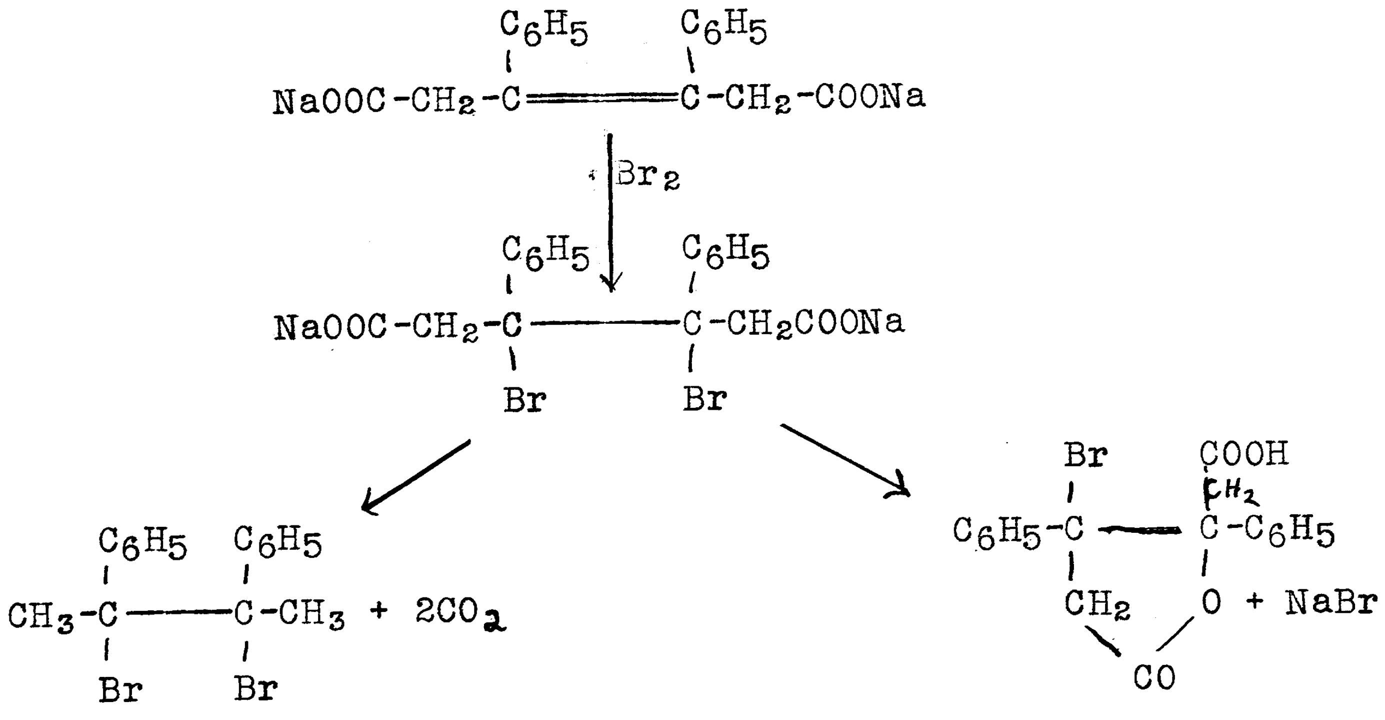
2,3-diphenylbutadiene, although he could prepare no characteristic derivatives. He attempted to brominate the diene, but was unsuccessful, attributing this to the proximity of the phenyl groups to the unsaturated carbon atoms.

Beschke (111) brominated an aqueous solution of the sodium salt of 2,3-diphenylbutene-1,4-dicarboxylic acid and obtained two products: a lactone, soluble in alkali, and another compound which was insoluble in alkali. The latter was recrystallized from glacial acetic acid in well-formed, lancet-shaped crystals, melting at 152°. Analysis indicated a formula of $C_{16}H_{16}Br_2$; he wrote the substance as XII.



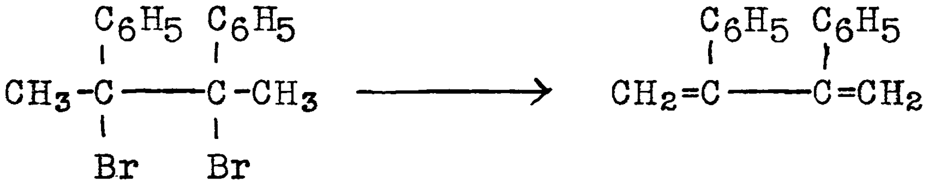
$$CH_3-\underset{Br}{\overset{C_6H_5}{C}}-\underset{Br}{\overset{C_6H_5}{C}}-CH_3$$

XII



XII

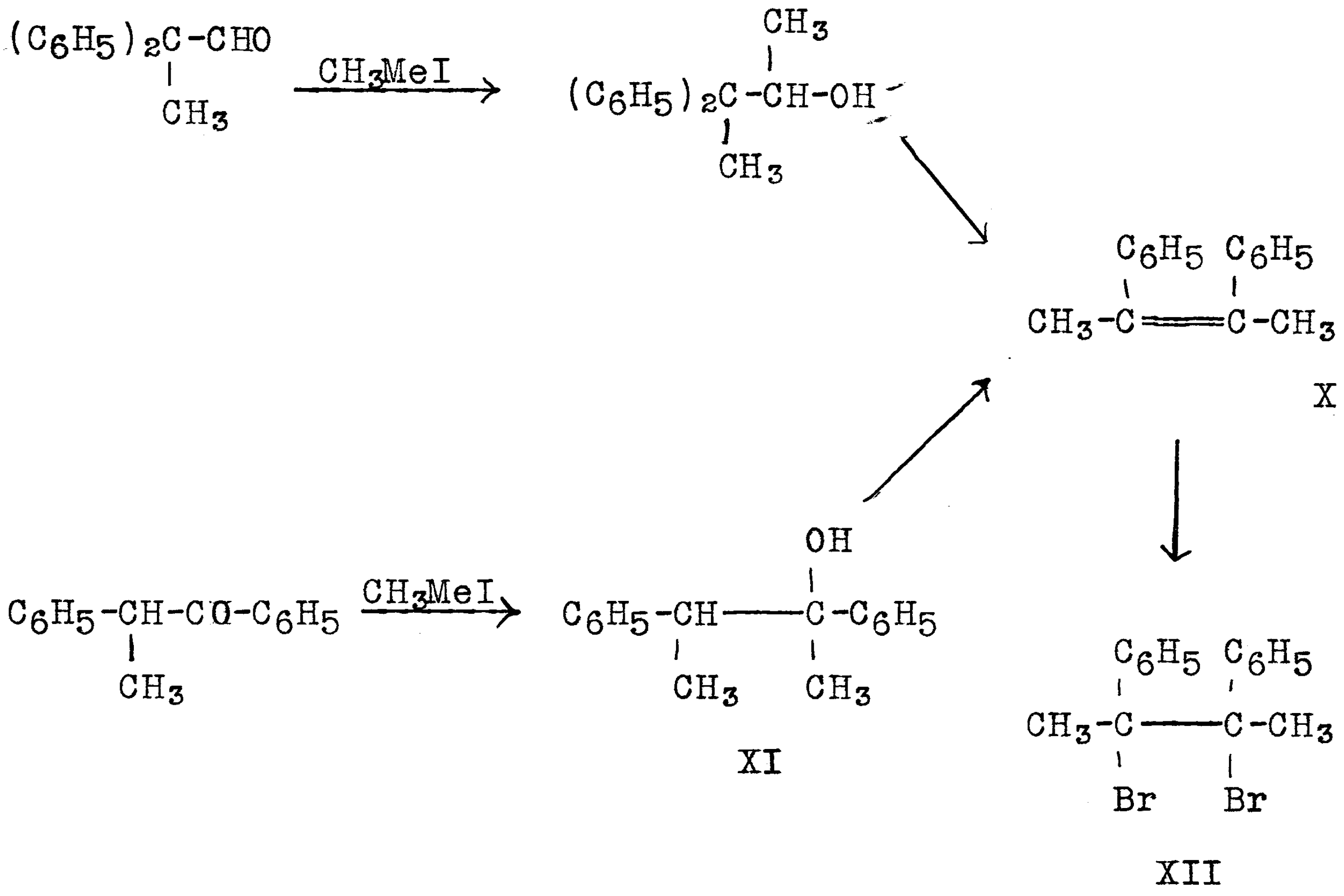
He attempted, unsuccessfully, to reduce the dibromide to the known 2,3-diphenylbutane (IX). Heating with zinc acetate or zinc dust in glacial acetic acid produced a colourless, water-insoluble oil, which slowly solidified. The halogen-free crystals melted at 48-9°. Beschke could not recrystallize this solid, and so concluded that it was the same compound as that obtained by Thörner and Zincke, which they also had not been able to recrystallize without polymerization. This would involve elimination of hydrogen bromide.



$$CH_3\text{-}\underset{Br}{\overset{C_6H_5}{C}}-\underset{Br}{\overset{C_6H_5}{C}}\text{-}CH_3 \longrightarrow CH_2=\overset{C_6H_5}{C}-\overset{C_6H_5}{C}=CH_2$$

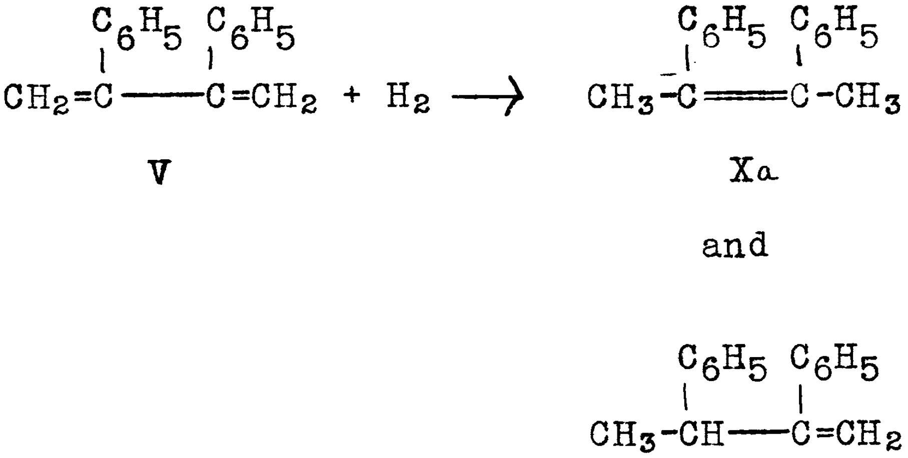
XII V

Lévy (112) prepared 2,2-diphenylbutanol-3 and 2,3-diphenylbutanol-2 (XI) by the action of methyl-magnesium iodide on the appropriate carbonyl compounds. Both these butanols, on distillation, yielded 2,3-diphenylbutene-2 (X), which added bromine readily to form 2,3-diphenyl-2,3-dibromobutane (XII). This compound melted at 150-5°.



Stobbe (113), in the course of his work on distyrenes, wished to synthesise this same saturated dibromide. He first prepared acetophenonepinacol (IV) by reduction of acetophenone with sodium amalgam. He stated that he had great difficulty in transforming the pinacol to the corresponding dibromide; but that, after many fruitless attempts, he succeeded by using acetyl bromide, followed by phosphorus pentabromide. The pinacol was treated with a large excess of acetyl bromide. A vigorous reaction occurred, and hydrogen bromide was evolved. When this reaction was over, phosphorus pentabromide was added to the cold yellow solution. More hydrogen bromide was then evolved, and the solution became a deep red, which changed to green after twelve hours standing. On pouring into dilute sodium carbonate solution a green oil separated, which soon set into a half-solid mass. Recrystallization from alcohol yielded fine needles with a silky lustre. Bromine analysis indicated $C_{16}H_{16}Br_2$, (calculated 43.46; found 43.28%). The dibromide melted at 140-5° with decomposition.

Ott (114) recorded that he had reduced 2,3-diphenylbutadiene, using one equivalent of hydrogen and a palladium-charcoal catalyst, and had obtained an oil which he considered to be a mixture of cis-dimethylstilbene (Xa) and 2,3-diphenylbutene-1.



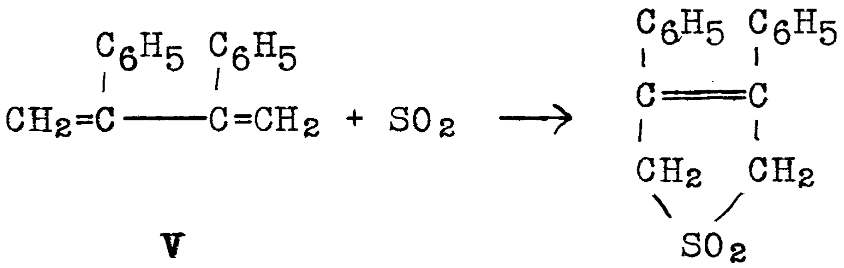
$$\underset{\text{V}}{CH_2=\overset{C_6H_5}{\overset{|}{C}}-\overset{C_6H_5}{\overset{|}{C}}=CH_2} + H_2 \longrightarrow \underset{\text{Xa}}{CH_3-\overset{C_6H_5}{\overset{|}{C}}=\overset{C_6H_5}{\overset{|}{C}}-CH_3}$$

and

$$CH_3-\overset{C_6H_5}{\overset{|}{CH}}-\overset{C_6H_5}{\overset{|}{C}}=CH_2$$

He stated that he would report later on this reduction, but no such report has appeared up to the present.

Backer (56) prepared 2,3-diphenylbutadiene by Johlin's method. He then dissolved it in a saturated etherial solution of sulphur dioxide, and heated the mixture at 100°. The solvent was evaporated, leaving the solid sulphone, which was recrystallized from alcohol. It melted at 184°, and the yield was 90%.



V

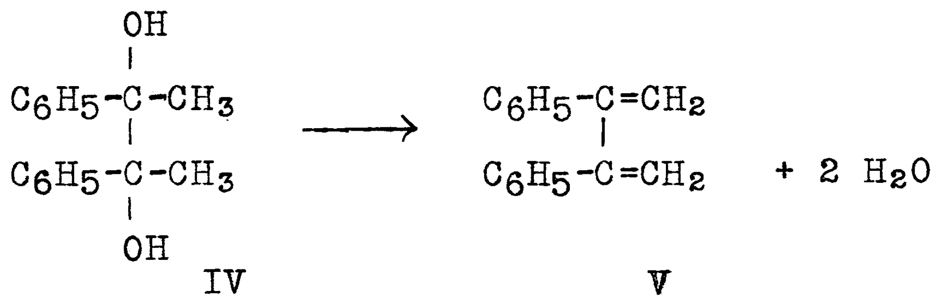
He found that selenium dioxide also added to the diene in a similar manner (57). Equivalent quantities of selenous acid and the diene were dissolved in chloroform, and shaken for five hours. The solvent was evaporated leaving a syrup. The selenone was separated from the unreacted diene by crystallization from a chloroform-petroleum ether mixture. The yield of selenone was only 4%. It melted at 89-90° with decomposition, forming a brown mass; was insoluble in water, and only slightly soluble in petroleum ether, ether, or benzene. It was comparatively unstable, beginning to decompose in a few days.

OUTLINE OF THE WORK, AND DISCUSSION OF RESULTS

2,3-Diphenylbutadiene

The first problem to be encountered in this work was the preparation of 2,3-diphenylbutadiene. The only procedure which had been previously described was that of Thörner and Zincke (109,110), but this method was found to give very unsatisfactory results.

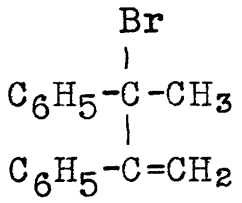
All the procedures which were investigated involved the dehydration of acetophenonepinacol (IV) to 2,3-diphenylbutadiene (V).



$$\begin{array}{c} \mathrm{OH} \\ | \\ \mathrm{C_6H_5{-}C{-}CH_3} \\ | \\ \mathrm{C_6H_5{-}C{-}CH_3} \\ | \\ \mathrm{OH} \end{array} \longrightarrow \begin{array}{c} \mathrm{C_6H_5{-}C{=}CH_2} \\ | \\ \mathrm{C_6H_5{-}C{=}CH_2} \end{array} + 2\ \mathrm{H_2O}$$

IV V

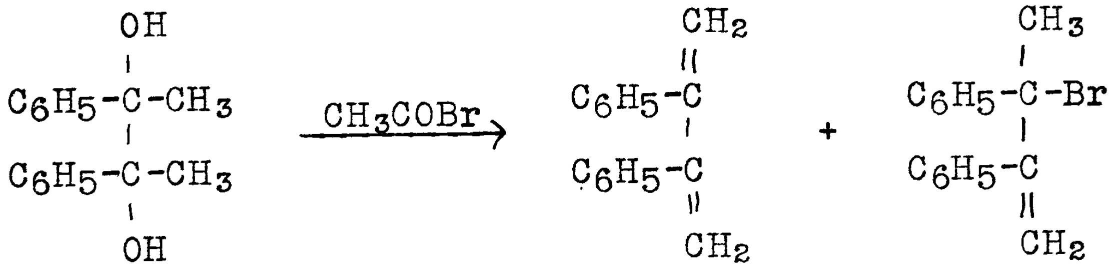
Acetyl bromide was found to give better results than any of the other dehydrating agents tried. The crystalline diene was not obtained directly from this reaction, which yielded, as a primary product, a crude greasy material, which could be purified to obtain a small amount of the diene in the form of an oil, and, as the main product, an unstable bromide; this was shown to be identical with the product obtained by adding hydrogen bromide to 2,3-diphenylbutadiene. Since this compound was a monobromide, and had the properties of a tertiary bromide, it was considered to be 2,3-diphenyl-2-bromobutene-3 (VI).



$$\begin{array}{rcl} & Br & \\ & | & \\ C_6H_5- & C & -CH_3 \\ & | & \\ C_6H_5- & C & =CH_2 \end{array}$$

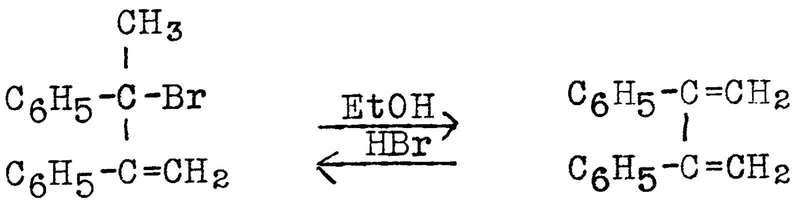
VI

The diene was prepared from the bromide (VI) by boiling the latter with dilute alcohol.



$$\begin{array}{rcl} & OH & \\ & | & \\ C_6H_5- & C & -CH_3 \\ & | & \\ C_6H_5- & C & -CH_3 \\ & | & \\ & OH & \end{array} \xrightarrow{CH_3COBr} \begin{array}{rc} & CH_2 \\ & \| \\ C_6H_5- & C \\ & | \\ C_6H_5- & C \\ & \| \\ & CH_2 \end{array} + \begin{array}{rcl} & CH_3 & \\ & | & \\ C_6H_5- & C & -Br \\ & | & \\ C_6H_5- & C & \\ & \| & \\ & CH_2 & \end{array}$$

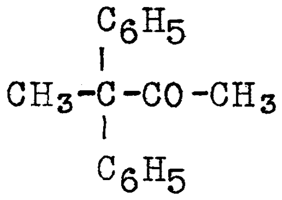
IV V VI



$$\begin{array}{rcl} & CH_3 & \\ & | & \\ C_6H_5- & C & -Br \\ & | & \\ C_6H_5- & C & =CH_2 \end{array} \overset{EtOH}{\underset{HBr}{\rightleftarrows}} \begin{array}{rcl} C_6H_5- & C & =CH_2 \\ & | & \\ C_6H_5- & C & =CH_2 \end{array}$$

VI V

Dehydration with acetic anhydride (Zincke's method) was carried out in a sealed tube (109,110), but, while the diene was usually obtained as an oil, the main crystalline product was the pinacolone (VII).



$$CH_3-\overset{\overset{C_6H_5}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-CO-CH_3$$

VII

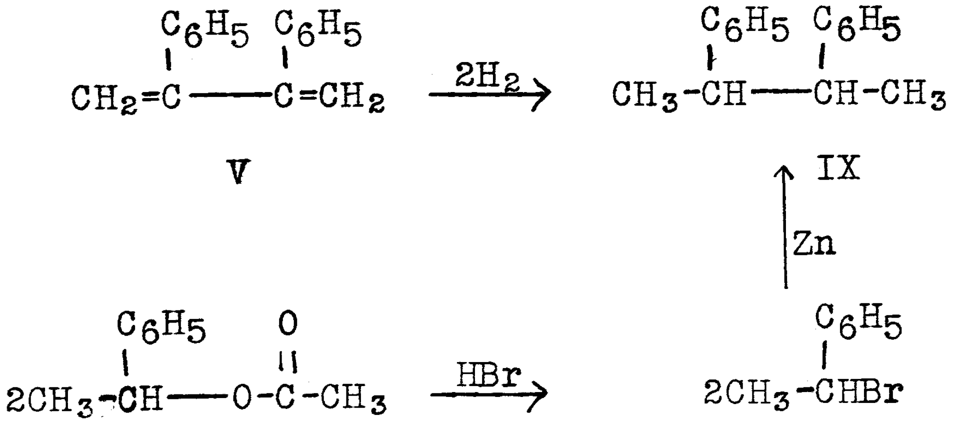
The yield of crystalline diene was greatly increased if antioxidants, such as phenyl-β-naphthylamine and copper acetate, were added to the reaction mixture.

Reduction

2,3-Diphenylbutadiene could not be reduced with sodium amalgam in alcohol. A faint anise-like odour was noted, but the diene was recovered almost quantitatively.

The diene was treated with sodium in liquid ammonia, and the product was extracted with boiling alcohol. On cooling, an insoluble solid was obtained. Analysis indicated that this was a bimolecular product. The alcoholic solution, on dilution, yielded another solid, which was purified and shown to be meso-2,3-diphenylbutane (IX) by comparison with an authentic sample. The oily residue from the evaporation of the filtrate possessed an anise-like odour.

Catalytic reduction using Adams'platinum catalyst (128) and excess hydrogen under pressure, yielded as the main product, 2,3-diphenylbutane (IX). This hydrocarbon was identical with that synthesised from α-bromoethylbenzene by the Würtz reaction (123).



$$CH_2{=}\overset{C_6H_5}{\overset{|}{C}}{-\!\!-}\overset{C_6H_5}{\overset{|}{C}}{=}CH_2 \xrightarrow{2H_2} CH_3{-}\overset{C_6H_5}{\overset{|}{CH}}{-\!\!-}\overset{C_6H_5}{\overset{|}{CH}}{-}CH_3$$

$$2CH_3{-}\overset{C_6H_5}{\overset{|}{CH}}{-\!\!-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xrightarrow{HBr} 2CH_3{-}\overset{C_6H_5}{\overset{|}{C}}HBr \xrightarrow{Zn} IX$$

The other reaction product was an oil which did not crystallize, and which possessed a very strong anise-like odour. Radziszewski (123) mentioned that his diphenylbutane had a pleasant odour, and on account of this it had been suggested as a constituent of insecticides (8). The oil may have been a mixture; containing the low melting isomeric butane (m.p.8°), the dienes and the butenes, in any proportions. The oil was completely volatile with steam, but the small amounts available prevented an extensive investigation.

The diene was also hydrogenated catalytically using one equivalent of hydrogen. Almost half the diene was recovered unchanged. The remaining product was a steam distillable oil from which no solid could be isolated. The same odour was noticed again. Ott (114) mentioned that he had reduced 2,3-diphenylbutadiene with one equivalent of hydrogen and a palladium-charcoal catalyst. He obtained an oil which he considered to be a mixture of cis-dimethylstilbene and 2,3-diphenylbutene-1. He stated that he intended to report more fully on this reaction. Such a report has not yet appeared, although Ott provided the samples of 2,3-diphenylbutadiene which von Auwers used for his determination of physical constants (115). In order to avoid possible duplication of effort in this particular field, these hydrogenation reactions were not investigated further.

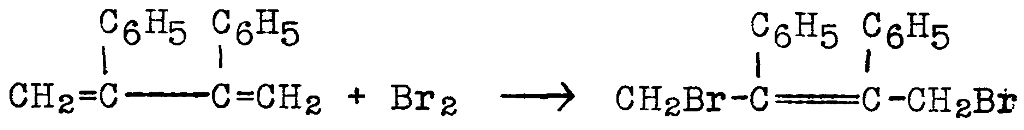
Bromination

Until this work was started, no derivatives of 2,3-diphenylbutadiene had been prepared, starting from the hydrocarbon. Johlin (110) had attempted to prepare some of them, but had been unsuccessful. In particular, he stated that the diene was not attacked by bromine (page 41); he attributed this inactivity to the position of the phenyl groups.

It has been found, however, that bromine will add readily to the diene at room temperature in a variety of solvents. Hydrogen bromide was always evolved, being especially noticeable towards the end of the reaction; this fact had already been noted during the bromination of other dienes (page 7). The crystalline product could be recrystallized from alcohol or acetone, and melted with decomposition at 145-7°; analysis showed that it was a dibromide. No evidence of a tetrabromide was ever secured.

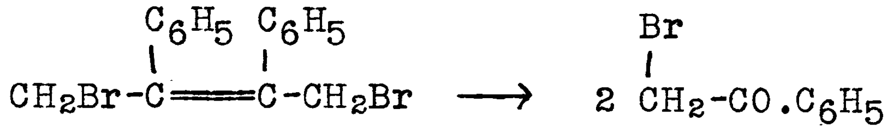
It seems probable that the compound which Johlin attempted to brominate was not the diene, but was the ketone (VII), which is so readily obtained from the dehydration reaction with acetic anhydride, if no antioxidants are present. This ketone will not add bromine at room temperature, and its melting point is only a few degrees lower than that of the diene.

In warm acetone solution the dibromide slowly decolorized permanganate. When subjected to ozonolysis the only decomposition product which could be identified was ω-bromoacetophenone. Formaldehyde could not be detected. This seems to indicate that the dibromide is 2,3-diphenyl-1,4-dibromobutene-2 (VIII).



$$CH_2{=}\overset{C_6H_5}{\overset{|}{C}}{-\!-\!-}\overset{C_6H_5}{\overset{|}{C}}{=}CH_2 + Br_2 \longrightarrow CH_2Br-\overset{C_6H_5}{\overset{|}{C}}{=\!=\!=}\overset{C_6H_5}{\overset{|}{C}}-CH_2Br$$

V VIII



$$CH_2Br-\overset{C_6H_5}{\overset{|}{C}}{=\!=\!=}\overset{C_6H_5}{\overset{|}{C}}-CH_2Br \longrightarrow 2\ \overset{Br}{\overset{|}{CH_2}}-CO.C_6H_5$$

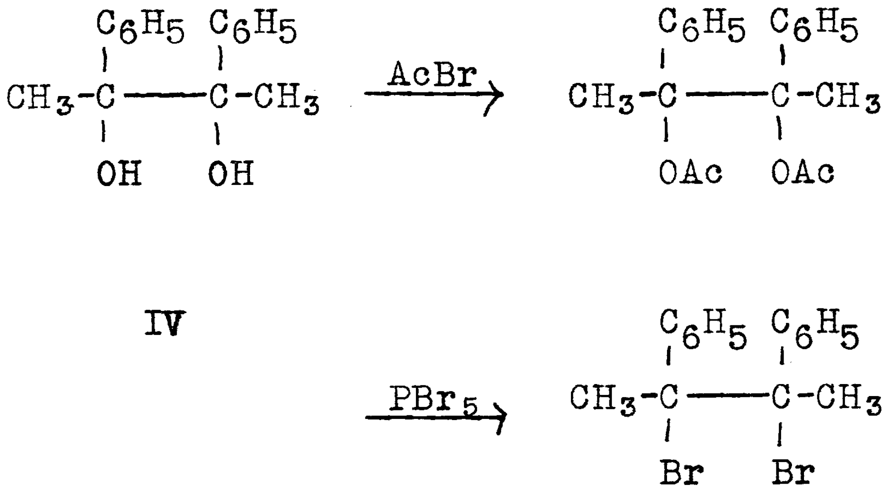
VIII

The dibromide (VIII) is not very useful for purposes of identification as it decomposes at its melting point. Its instability is also shown by the lowering in melting point of samples which have remained for some time exposed to moist air, and by the fact that when it is dissolved in ethyl alcohol, on addition of alcoholic silver nitrate, the solution will give an immediate precipitate of silver bromide.

The diene could be regenerated from the dibromide

(VIII) by treating it with zinc dust in acetone or acetic acid. It was very convenient to prepare the relatively stable dibromide from the unstable diene, and then, by zinc dust treatment, to regenerate the diene as required.

Two dibromides have already been prepared with properties somewhat similar to those of the 1,4-dibromide of 2,3-diphenylbutadiene (VIII). Both these compounds were considered to be 2,3-dibromo-2,3-diphenylbutane (XII) by the workers who made them, although their properties were not very similar. The first to be prepared was a compound melting at 140-145° with decomposition (fine needles, silky lustre). This was made by Stobbe (113 and page 43) who proposed the following series of reactions to account for its preparation.



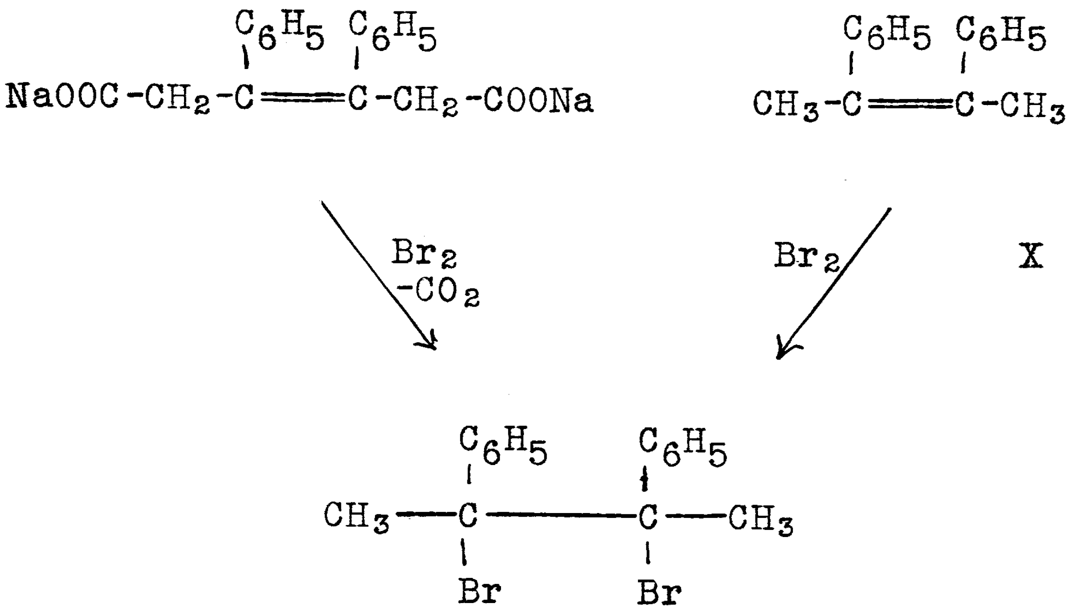
$$\underset{\text{IV}}{CH_3-\overset{\overset{C_6H_5}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{C_6H_5}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3} \xrightarrow{AcBr} CH_3-\overset{\overset{C_6H_5}{|}}{\underset{\underset{OAc}{|}}{C}}-\overset{\overset{C_6H_5}{|}}{\underset{\underset{OAc}{|}}{C}}-CH_3 \xrightarrow{PBr_5} \underset{\text{XII}}{CH_3-\overset{\overset{C_6H_5}{|}}{\underset{\underset{Br}{|}}{C}}-\overset{\overset{C_6H_5}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3}$$

IV

XII

The second compound to be prepared was that described by

Beschke (111 and page 41), and later by Lévy (112 and page 42).



$$NaOOC\text{-}CH_2\text{-}\overset{C_6H_5}{\overset{|}{C}}{=}\overset{C_6H_5}{\overset{|}{C}}\text{-}CH_2\text{-}COONa \xrightarrow[-CO_2]{Br_2} CH_3\text{-}\underset{Br}{\underset{|}{\overset{C_6H_5}{\overset{|}{C}}}}\text{-}\underset{Br}{\underset{|}{\overset{C_6H_5}{\overset{|}{C}}}}\text{-}CH_3 \xleftarrow{Br_2} CH_3\text{-}\overset{C_6H_5}{\overset{|}{C}}{=}\overset{C_6H_5}{\overset{|}{C}}\text{-}CH_3$$

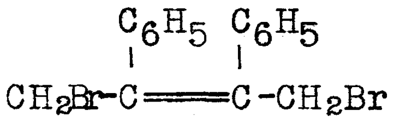
X

XII

This solid was obtained in lancet-shaped crystals melting at 152°. Beschke was unsuccessful in reducing this compound (XII) to the known 2,3-diphenylbutane (IX), but, on heating with zinc dust or zinc acetate in glacial acetic acid, he obtained an oil from which halogen-free crystals slowly formed; these melted at 48-9°. When he attempted to recrystallize this compound he obtained an oil.

When the dibromide (VIII) was compared with the compounds just described, it was found to resemble Stobbe's compound much more closely than it did the dibromide made by

Beschke and Lévy. Since ozonolysis had shown that the dibromide (VIII) was unsaturated and had the formula,



$$CH_2Br-\overset{C_6H_5}{\overset{|}{C}}=\overset{C_6H_5}{\overset{|}{C}}-CH_2Br$$

VIII

it seemed certain that the formula (XII), ascribed to this compound by Stobbe, was incorrect.

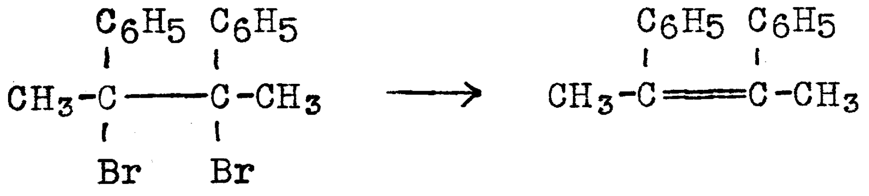
In order to identify these dibromides with greater certainty, both Stobbe's and Beschke's work was repeated, and the melting points of the three dibromides were compared. They were all recrystallized from acetone and formed white crystals, all of which appeared to be similar (although no microscopic investigation was carried out).

Dibromide	Melting Point	Condition of Product
A From diene	142-146° (also 145-147°)	Brown liquid
B Beschke's	142-144°	Brown liquid with evolution of bubbles.
C Stobbe's	145-147°	Brown liquid
A + B	139-141°	
A + C	142-146°	
B + C	138-142°	

The melting point values for A are for the freshly prepared compound. Unless it was kept in a vacuum dessicator this dibromide underwent some change which lowered its melting point somewhat - in some cases as much as ten degrees.

Since decomposition occurs so readily, these melting point values are not of much significance but, if they indicate anything, it is that A and C are identical, and differ from B.

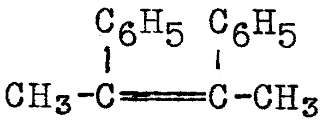
The identity of A and C was shown by treating them both with zinc dust in acetone, and obtaining 2,3-diphenylbutadiene in each case. Beschke's dibromide, B, when treated in this manner, formed an oil from which no crystals could be obtained. While zinc in acetic acid might remove hydrogen bromide to form 2,3-diphenylbutadiene, as Beschke considered it did (page 42); it is more likely that bromine only would be removed.



$$CH_3-\underset{Br}{\overset{C_6H_5}{C}}-\underset{Br}{\overset{C_6H_5}{C}}-CH_3 \longrightarrow CH_3-\overset{C_6H_5}{C}=\overset{C_6H_5}{C}-CH_3$$

XII X

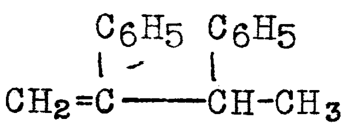
Ott's work (114) on the preparation of all three possible isomeric 2,3-diphenylbutenes,


$$CH_3-\overset{C_6H_5}{\overset{|}{C}}=\overset{C_6H_5}{\overset{|}{C}}-CH_3$$

X

cis and trans

and


$$CH_2=\overset{C_6H_5}{\overset{|}{C}}-\overset{C_6H_5}{\overset{|}{C}}H-CH_3$$

XL

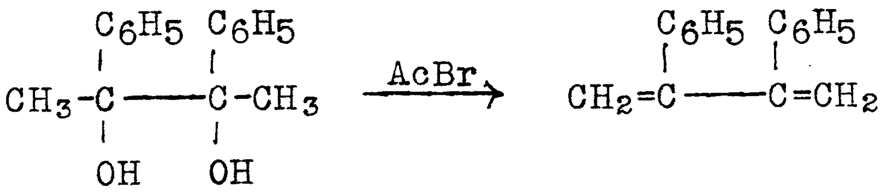
indicates that mixtures of such 2,3-diphenylbutenes may be oils, and that crystals of crude cis-2,3-diphenylbutene-2, melting over a range starting at 50°, might be obtained from such mixtures. Ott did not isolate the 1,2-butene (XL), so its presence in such oils is not certain.

It must also be remembered that, in the case of the dibromides, isomers are possible. 2,3-Diphenyl-1,4-dibromobutene-2 (VIII) can exist in either the cis or trans form. This may account for the changes in the melting point of dibromide A on standing. 2,3-Diphenyl-2,3-dibromobutane can also exist in two stereoisomeric forms; one of these is Beschke's dibromide (XIIb).

These two stereoisomeric dibromides were synthesised by brominating cis- and trans-dimethylstilbene (Xa and Xb). They differed from the unsaturated dibromide (VII), prepared from the diene, or by Stobbe's method, in being unstable in hot alcoholic solution; attempts to recrystallize these compounds from alcohol resulted in the formation of cis-dimethylstilbene (Xa) in each case. The crude product melted at 46-48°. This indicates that Beschke's dibromide was the 2,3-

diphenyl-2,3-dibromobutane (XIIb), m.p. 149-152°, formed by brominating trans-dimethylstilbene (Xb).

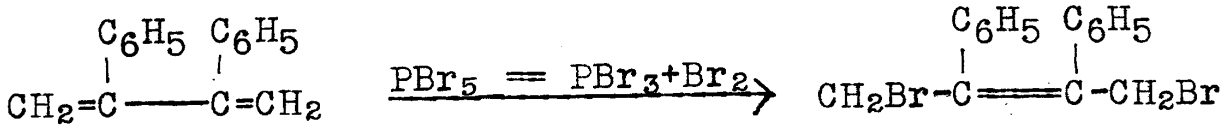
Since Stobbe's dibromide is actually the unsaturated 1,4-dibromide (VIII), his mechanism for the reaction of acetyl bromide and phosphorus pentabromide with the diene is incorrect. He suggested a diacetate as an intermediate (page 53), but it is now known (145) that tertiary alcohols react with acyl halides at room temperature to yield tertiary halides rather than esters. The tertiary bromides (XIIa and XIIb), which might be formed here, however, were found to be unstable to treatment with acetyl bromide, and were never isolated from the reaction product. In this reaction, therefore, dehydration must have occurred.



$$CH_3-\underset{OH}{\overset{C_6H_5}{C}}-\underset{OH}{\overset{C_6H_5}{C}}-CH_3 \xrightarrow{AcBr} CH_2=\overset{C_6H_5}{C}-\overset{C_6H_5}{C}=CH_2$$

IV V

Since phosphorus pentabromide always acts as $PBr_3 + Br_2$, the second step in the reaction, addition of bromine to the diene would be expected to give the 1,4- addition product (VIII), while Beschke's dibromide (XIIb) would not be formed



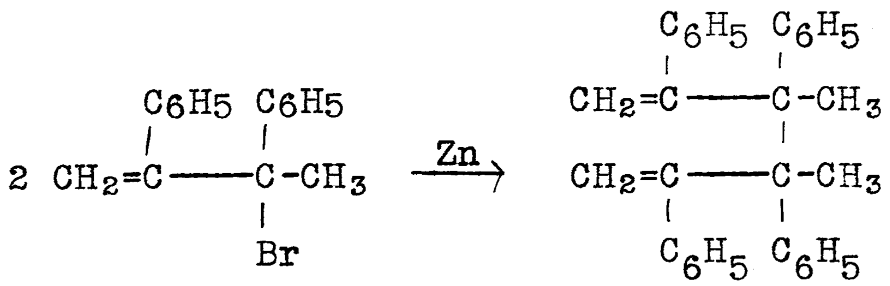
$$CH_2=\overset{C_6H_5}{C}-\overset{C_6H_5}{C}=CH_2 \xrightarrow{PBr_5 = PBr_3+Br_2} CH_2Br-\overset{C_6H_5}{C}=\overset{C_6H_5}{C}-CH_2Br$$

V VIII

This step was confirmed by carrying out the same reaction, but substituting bromine for phosphorus pentabromide. A solid dibromide was formed, which was identical with that obtained from the diene, or from Stobbe's preparation (VIII); debromination with zinc dust in acetone yielded the diene (V). In order to get further insight into the mechanism of Stobbe's reaction, the process was stopped at the end of the first stage, after the pinacol (IV) had been treated with excess acetyl bromide. Copious fumes of hydrogen bromide were evolved, and the greasy product was recrystallized from petroleum ether. Crystals of the hydrogen bromide addition product (VI) were obtained as the main product. On evaporation of the filtrate, an oil remained, which was shown to contain the diene (V) by bromination to form the dibromide (VIII). These reactions seem to indicate that acetyl bromide dehydrates the pinacol, and the resulting diene reacts with the hydrogen bromide formed during the reaction, to form the monobromide (VI). If bromine is present however, the dibromide (VIII) is the addition product.

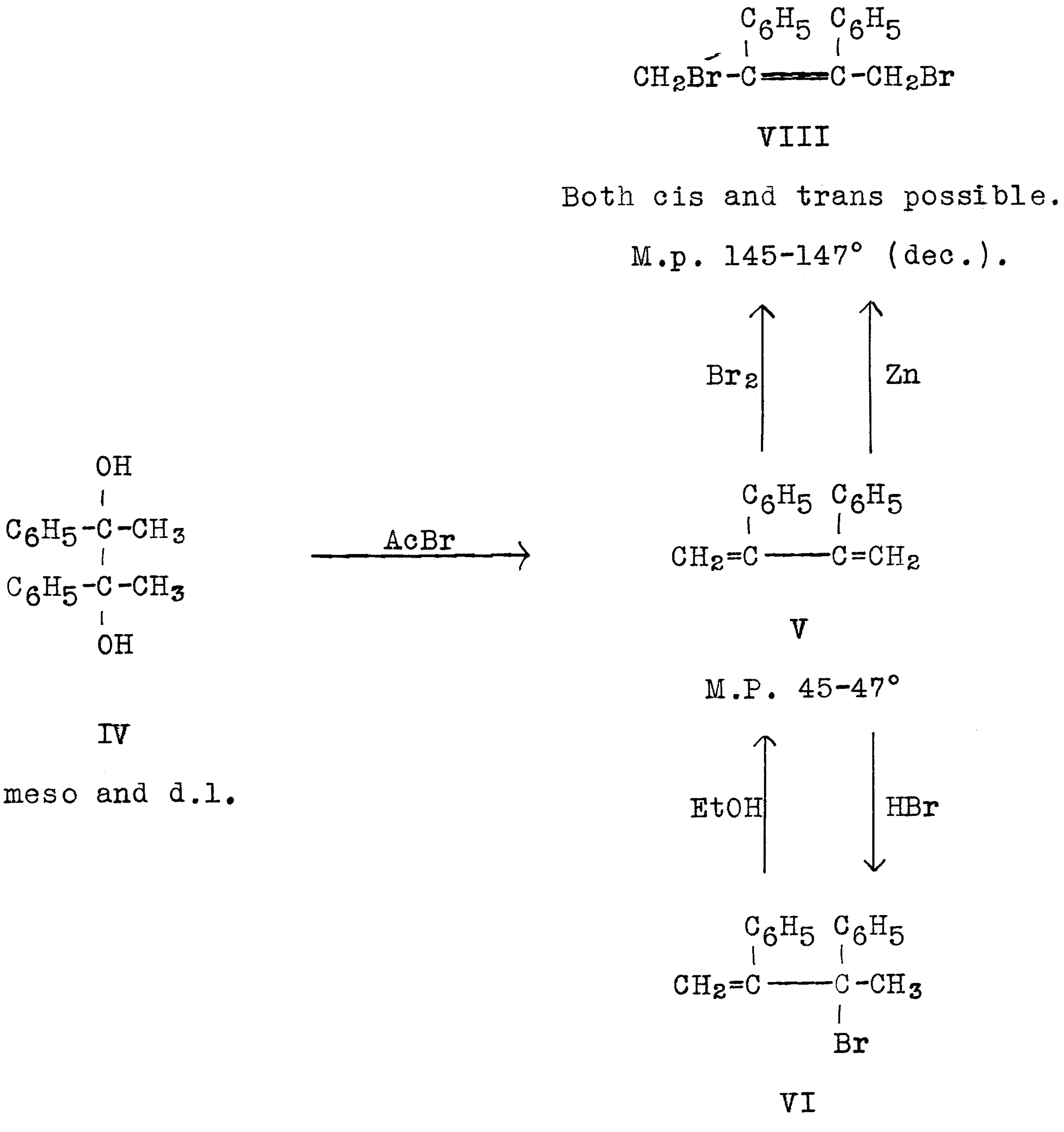
Hydrogen Bromide

The preparation and properties of the hydrogen bromide addition product (VI) have already been discussed in some detail. This compound was shown to be a monobromide, and its reactions suggest that it is a tertiary bromide, 2,3-diphenyl-2-bromobutene-3. It was most easily prepared by treating acetophenonepinacol with acetyl bromide, but was also formed by the direct addition of hydrogen bromide to a chloroform solution of the diene. Treatment of the monobromide (VI) with zinc dust in acetone gave an oil, from which a solid was separated by addition of acetone. This solid melted at 204° and contained no halogen. Analysis indicated that it was the bimolecular compound.



$$2\ CH_2{=}\overset{C_6H_5}{C}-\underset{Br}{\overset{C_6H_5}{C}}-CH_3 \xrightarrow{Zn} \begin{array}{l} CH_2{=}\overset{C_6H_5}{C}-\overset{C_6H_5}{C}-CH_3 \\ \qquad\qquad\quad\ | \\ CH_2{=}\underset{C_6H_5}{C}-\underset{C_6H_5}{C}-CH_3 \end{array}$$

The reactions involving the bromides are summarized below.



VIII

Both cis and trans possible.

M.p. 145-147° (dec.).

IV

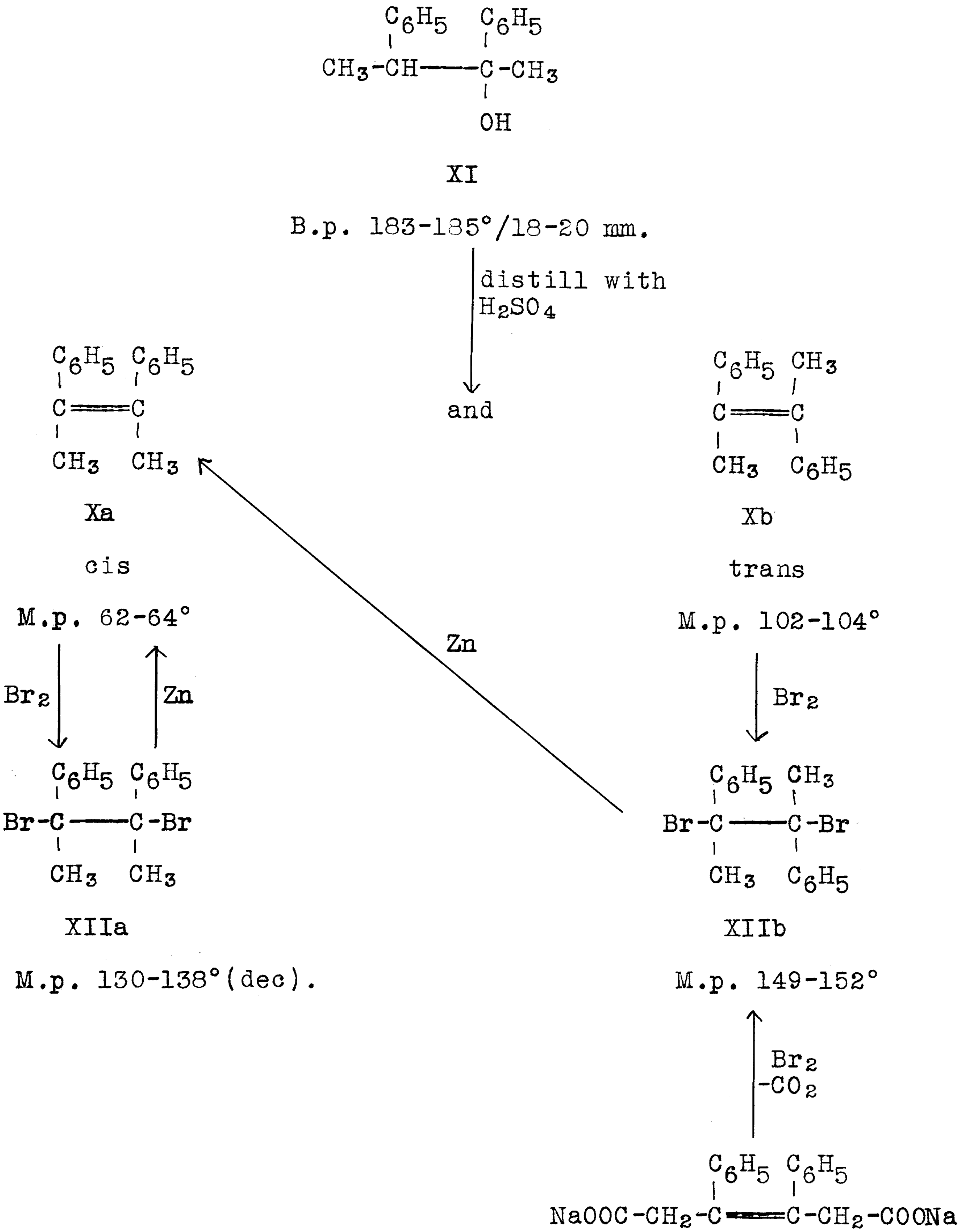
meso and d.l.

V

M.P. 45-47°

VI

M.p. 78°

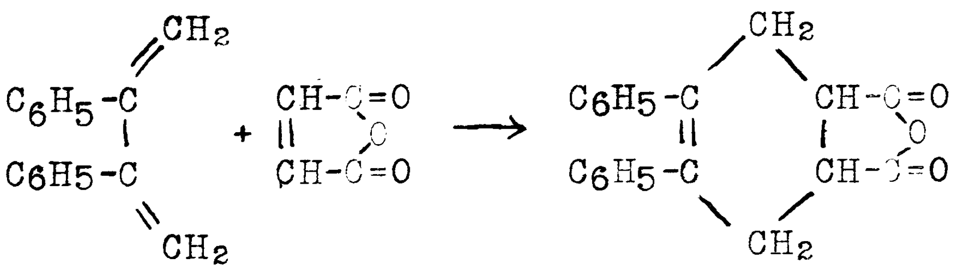

XI
B.p. 183-185°/18-20 mm.
distill with H_2SO_4
and
Xa
cis
M.p. 62-64°
Xb
trans
M.p. 102-104°
Br_2
Zn
Zn
Br_2
XIIa
M.p. 130-138°(dec).
XIIb
M.p. 149-152°
Br_2
$-CO_2$
NaOOC-CH_2-C=C-CH_2-COONa

The Diene Synthesis

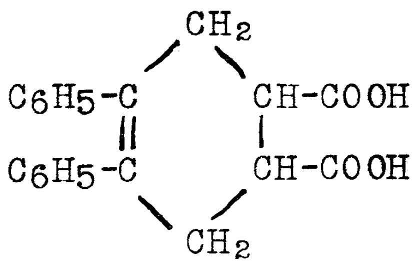
2,3-Diphenylbutadiene reacted readily **with** maleic anhydride and with α-naphthoquinone. Other diene synthesis addends which were used either did not react at all, or did so with difficulty. Since the course of the diene synthesis depends to a large extent on the conditions employed, it is quite possible that under different conditions, the diene may react more readily with these other compounds.

Since none of the addition products had been synthesised before, it was necessary to prove their structure. In the case of the most thoroughly studied reaction - that with maleic anhydride, this involved considerable difficulty.

The diene, on treatment with maleic anhydride and subsequent hydrolysis, formed an acid, which was insoluble in water, and which analysed for a diphenyltetrahydrophthalic acid. This compound would be expected to be 4,5-diphenyl-1,2,3,6-tetrahydrophthalic acid (I).



V XV



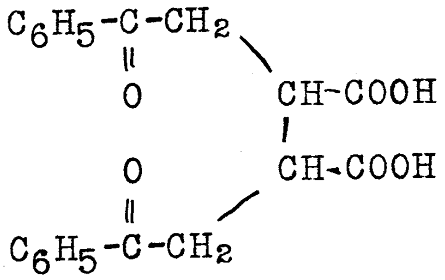
I

The acid melts at 172-3°, and seems to be much more stable than the other tetrahydrophthalic acids which have been reported. This may be due to the stability of the stilbene system, which lessens the tendency to become conjugated by dehydrogenation.

The usual methods for degrading such acids to the corresponding aromatic hydrocarbons are either treatment with potassium ferricyanide (100), or distillation of the calcium salt with lime and zinc dust (99). Both these methods were unsatisfactory in this case; distillation with lime and zinc dust seemed to decompose the acid, and only resinous products were obtained. The diene synthesis was probably reversed by this treatment. No trace of o-diphenylbenzene (III) was found in either case.

Very small quantities of o-diphenylbenzene were occasionally produced by fusing the acid (I) with potassium hydroxide. The main product of this reaction, however, was always the acid (II) considered to be 4,5-diphenylphthalic acid.

The acid (I) from the diene synthesis was not attacked by permanganate, and as the degradation product

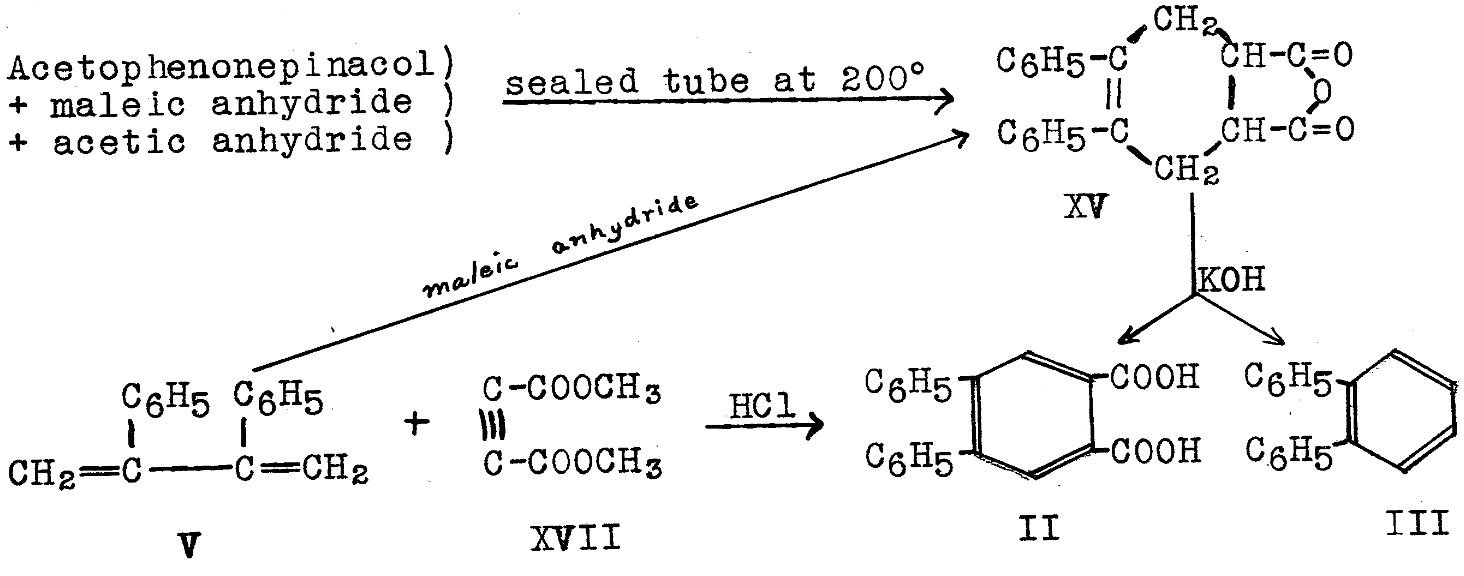


is unknown, further oxidation reactions were not investigated.

Decarboxylation with copper powder in quinoline (124), by fusion with sodamide, or by zinc dust distillation was in each case unsuccessful. Heating the sodium salt of the acid (I) with soda lime decomposed the acid, and no products could be isolated.

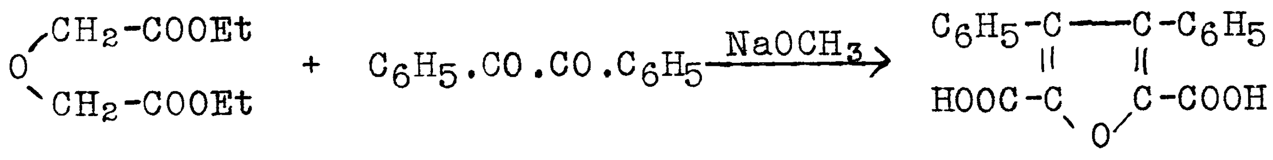
This acid, and those formed from it by fusion with potassium hydroxide, formed dyes when fused with resorcinol and a drop of concentrated sulphuric acid (125). Like fluorescein, these dyes could be brominated and iodinated to give dyes with a deeper colour. These new dyes had a browner shade than their unphenylated analogues, ranging from pale orange to tans and rust reds. A few were fairly fast to washing, but they were not fast to prolonged exposure to sunlight. They were not further investigated.

Acetylenedicarboxylic ester (XVII) added to the diene, but the yields were very low. The product, when boiled with hydrochloric acid, gave small amounts of an acid which proved to be identical with that isolated from the alkaline fusion.

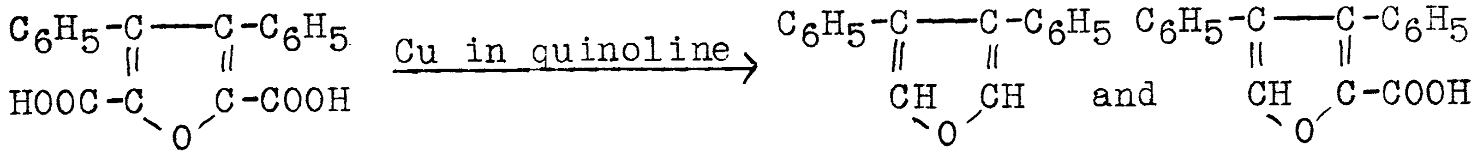


The aromatic acid (II) was also synthesised from 3,4-diphenylfuran (XVIII) and maleic anhydride. 3,4-Diphenylfuran was prepared by decarboxylation of the acid obtained from the condensation of benzil with diglycolic ester (XIX).

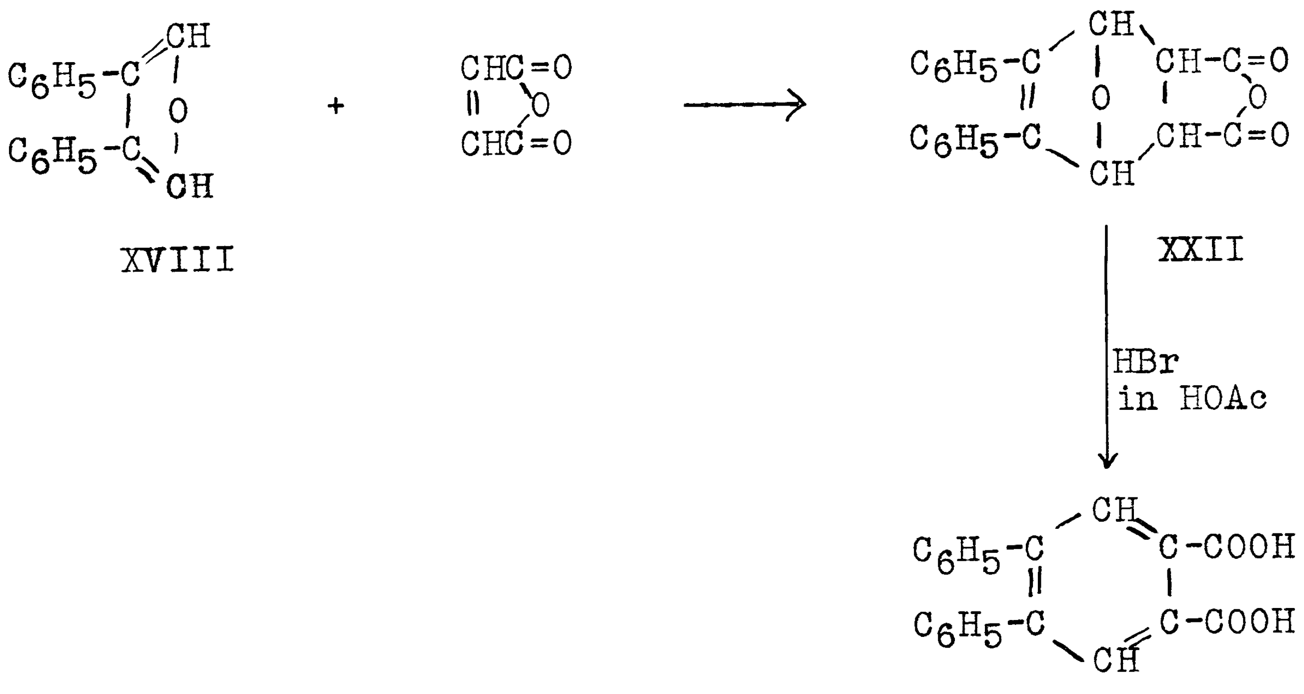
$2CH_2ClCOOH + Ba(OH)_2 \longrightarrow HOOCCH_2OCH_2COOH \longrightarrow$ ethyl ester.



XIX XX



XX XVIII XXI



XVIII XXII II

These reactions all seemed to indicate that the acid produced by alkaline fusion was the aromatic acid. This was also confirmed by the fact that it was unchanged when heated with selenium for 3-1/2 hours at 325°. The original acid (I) obtained from the diene synthesis might have been either cis- or trans- 4,5-diphenyl-1,2,3,6-tetrahydrophthalic acid. Unless recrystallized many times from acetic acid, it melted over a range - anywhere between 160° and 170°. As originally isolated, it generally melted about 160°, although considerable shrinkage took place before that. This low-melting acid dissolved in alkali to form a yellow solution. Samples which had been recrystallized from acetic acid formed a colourless solution when dissolved in aqueous sodium hydroxide[*]. In the case of the

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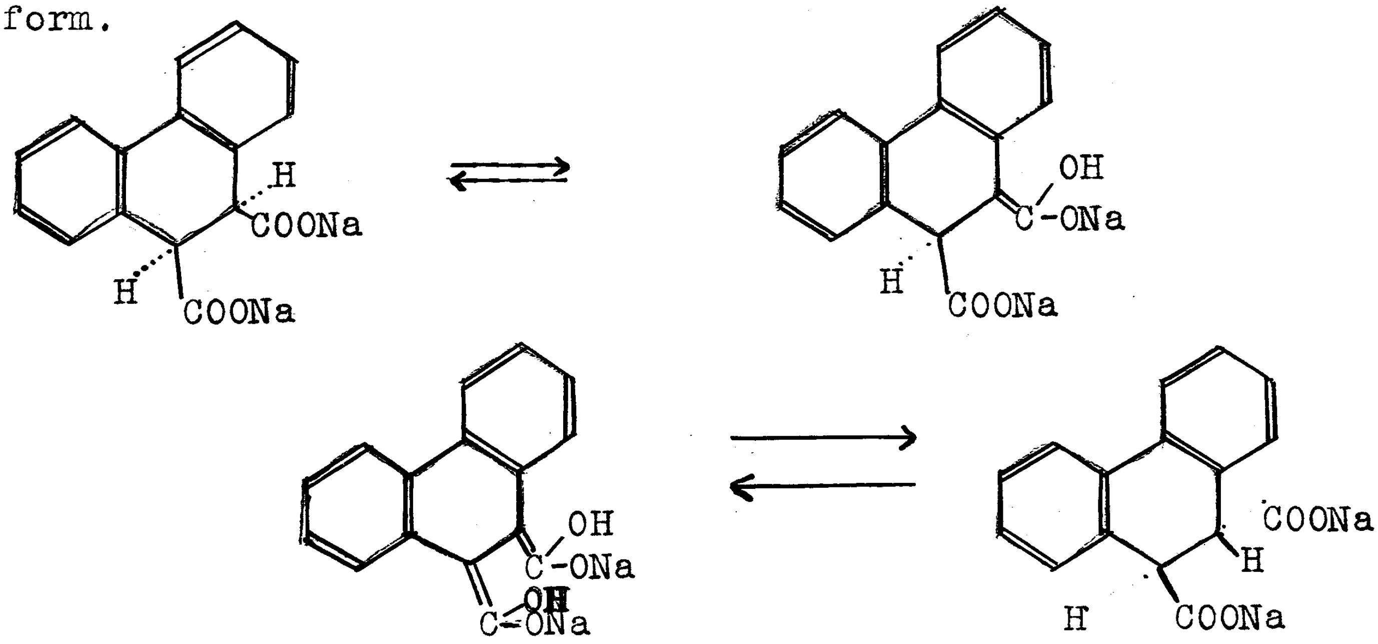
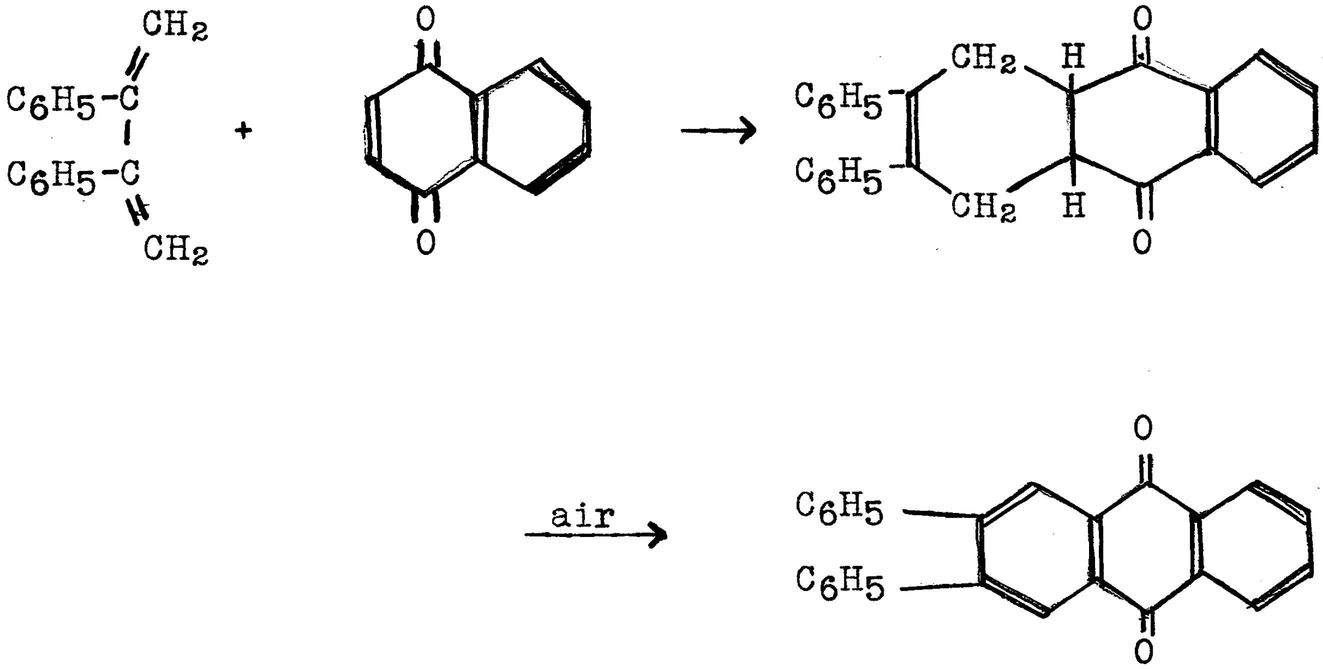
[*] Adams (126) pointed out that cis-9,10-dicarboxy-9,10-dihydrophenanthrene (XXIII) formed an orange solution in dilute sodium hydroxide, while the trans form XVI gave no colour when dissolved in alkaline solution. Adams' cis-dihydro acid fused at 196°, solidified, and then melted completely at 235-240°. The trans-acid, when pure, melted over a range, 235-242°, with decomposition. Adams explained the yellow colour of the sodium salt of the cis-acid as being due to enolization. Warming the cis-acid in dilute alkali, or heating with glacial acetic acid, converted it to the trans form.



diphenyltetrahydrophthalic acids (I) there was not any definite evidence of a cis form. The acid was precipitated by pouring a solution of its sodium salt into concentrated hydrochloric acid. Boiling was generally required to coagulate the acid. This would be expected to convert the cis-acid into the trans form. The low melting point, and yellow sodium salt might be due to small quantities of cis-acid, but they might also be due to some other impurity.

2,3-Diphenylbutadiene reacted with α-naphthoquinone in boiling xylene to give a product which, when dissolved in hot acetone, yielded a yellow quinone (XXIV).



XXIV

This quinone dissolved in concentrated sulphuric acid to form a brown solution from which it could be recovered by dilution. Reduction with sodium hydrosulphite in dilute methyl alcohol produced a green compound, which was soluble in water. Oxidation of this green solution with sodium perborate regenerated the yellow quinone. Reduction of the quinone with zinc in aqueous sodium hydroxide produced a red solution. The yellow quinone was slowly regenerated by passing air through the acidified solution.

This quinone (XXIV) was not the only product of the reaction with the diene. A dark red-brown solid was also formed, which dissolved in ethyl alcohol to form a crimson solution. Addition of alcoholic alkali turned this to a brilliant blue, which became greenish on standing. On oxidation by the air, and acidification with concentrated hydrochloric acid, a red-purple precipitate was formed which was recrystallized from dilute acetic acid.

This compound dissolved in concentrated sulphuric acid to form a brown solution from which it was regenerated by dilution. Sodium hydrosulphite in dilute methyl alcohol yielded a yellow-brown compound which was soluble in water. Oxidation with sodium perborate produced a turbid solution from which no crystals could be obtained. Zinc in alkali gave a red solution from which the original red solid was precipitated on acidification.

This red compound seemed to have the properties of a hydroxy-quinone. Analytical figures indicated a formula

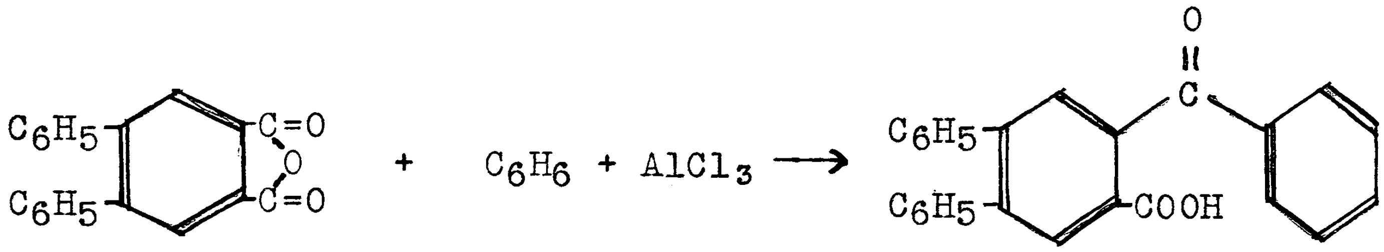
$C_{26}H_{14}O_5$, but the sample may not have been pure. It was very difficult to recrystallize, and, when it did come down, was an amorphous powder. The melting points of different samples varied greatly, and decomposition was always found to occur. Preliminary investigations seemed to show that 1,4-diphenylbutadiene forms a similar red compound with α-naphthoquinone.

Benzoquinone yielded complex tarry mixtures with the diene, from which no pure compounds could be isolated. β-Benzoylacrylic acid seemed to polymerize, rather than add to the diene.

Acetylene did not add to the diene in boiling naphthalene - nor did benzoylphenylacetylene in boiling xylene. An attempt was made to add phenylacetylene, and in one instance, on vacuum distillation of the reaction product, a fraction, b.p. 270-80° at 20 mm., was obtained, from which separated a few crystals which melted at 140-155°. No more of this solid could be prepared.

Miscellaneous Reactions

An attempt was made to synthesise an o-benzoylbenzoic acid by treating the anhydride of the aromatic acid (II) with benzene and aluminium chloride.

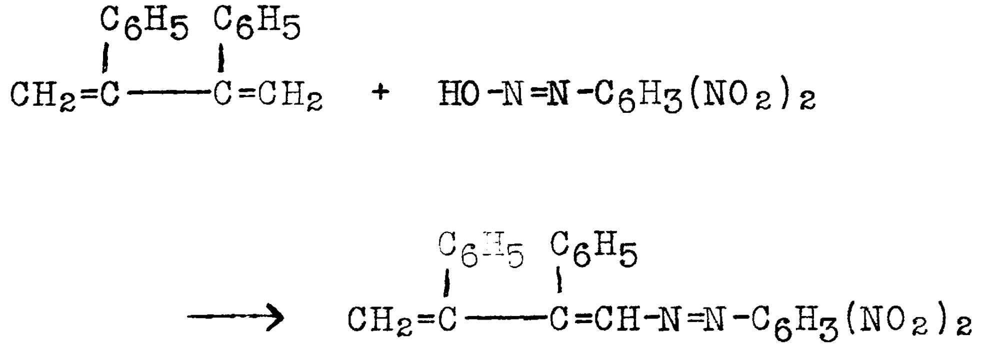


II

XXV

No such acidic compound could be isolated however. This compound (XXV) had already been prepared by Allen and Spanagel (103).

The diene (V) coupled with diazotized 2,4-dinitroaniline to give a red-brown solid.

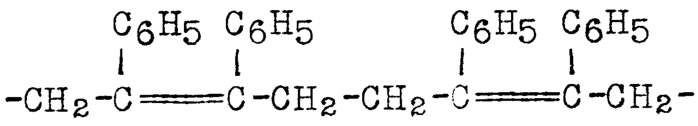


$$\overset{C_6H_5}{\overset{|}{CH_2=C}}-\overset{C_6H_5}{\overset{|}{C=CH_2}} + HO-N=N-C_6H_3(NO_2)_2$$

$$\longrightarrow \overset{C_6H_5}{\overset{|}{CH_2=C}}-\overset{C_6H_5}{\overset{|}{C=CH-N=N-C_6H_3(NO_2)_2}}$$

Backer and Strating reported adding sulphur dioxide to 2,3-diphenylbutadiene (56, and page 45). They heated the diene with a saturated ethereal solution of sulphur dioxide at 100°. This work was repeated; the solution was heated in a sealed tube at 100° for one hour, but, under these conditions, the diene was recovered unchanged.

The ribbon of polymerized material, which was often formed during the preparation of the diene by the sealed tube reaction, was distilled under reduced pressure. Acetophenone and an oil, which contained trans-dimethylstilbene (Xb), were produced. Trans-dimethylstilbene yields no acetophenone under similar conditions, so the ketone must have been produced from the polymer, possibly from the ends of the chain. The production of dimethylstilbene seems to indicate that the polymer is a linear type,



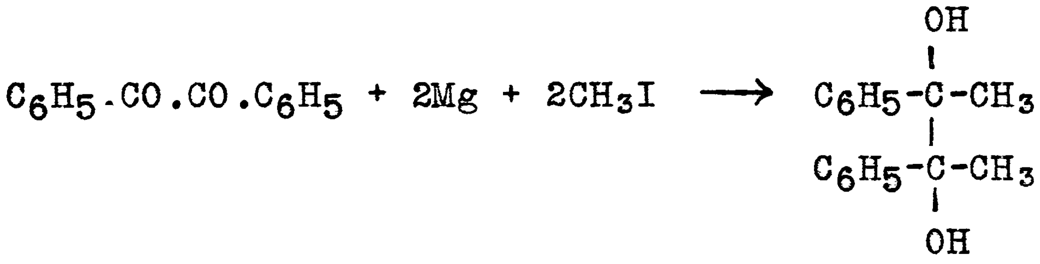
$$-CH_2-\overset{\overset{C_6H_5}{|}}{C}=\overset{\overset{C_6H_5}{|}}{C}-CH_2-CH_2-\overset{\overset{C_6H_5}{|}}{C}=\overset{\overset{C_6H_5}{|}}{C}-CH_2-$$

but the course of decomposition of such a polymer is not clear.

EXPERIMENTAL PART

Introduction

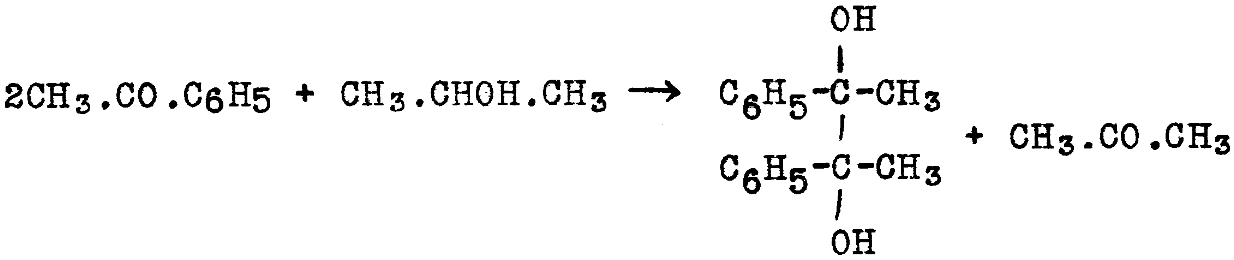
There are two reactions for securing the necessary pinacol (IV); use of the Grignard reagent with benzil (110, 118, 120),



$$C_6H_5.CO.CO.C_6H_5 + 2Mg + 2CH_3I \longrightarrow \begin{array}{c} OH \\ | \\ C_6H_5-C-CH_3 \\ | \\ C_6H_5-C-CH_3 \\ | \\ OH \end{array}$$

IV

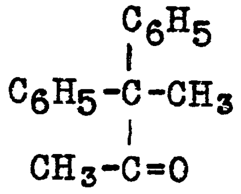
and bimolecular reduction, using isopropyl alcohol in the sunlight (119).



$$2CH_3.CO.C_6H_5 + CH_3.CHOH.CH_3 \longrightarrow \begin{array}{c} OH \\ | \\ C_6H_5-C-CH_3 \\ | \\ C_6H_5-C-CH_3 \\ | \\ OH \end{array} + CH_3.CO.CH_3$$

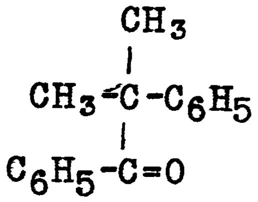
IV

In both instances the desired product crystallized slowly from the yellow oil which was first formed. It was thought that the residual oil might be a ketone formed by dehydration and rearrangement of the pinacol.



$$\begin{array}{c} C_6H_5 \\ | \\ C_6H_5\text{-}C\text{-}CH_3 \\ | \\ CH_3\text{-}C{=}O \end{array}$$

or



$$\begin{array}{c} CH_3 \\ | \\ CH_3\text{-}C\text{-}C_6H_5 \\ | \\ C_6H_5\text{-}C{=}O \end{array}$$

The oil however, would not form an oxime or semicarbazone, and was unchanged when treated with sodium hypobromite. Its nature is still undetermined.

The pinacol obtained was a mixture of the two stereoisomers, which melted at 83-114°; the two isomers are reported to melt at 116-7° and 122° respectively when pure. The second method required four months' exposure to the sunlight in the summer, and about eight months' in the other seasons; but it was found to be more convenient than the Grignard reaction, because of the inexpensive starting materials and the small amount of attention required.

<u>Acetophenonepinacol</u> (IV).

A mixture of the two stereoisomers, m.p. 83-114°, was obtained in 56% yield by the action of methyl magnesium iodide on benzil. Benzil (6 g.) was added to a solution of 2.2 g. of magnesium and 15 g. of methyl iodide in dry ether. The mixture was stirred mechanically and cooled, then gradually warmed and refluxed for 1-1/2 hours. After allowing it to stand over night, the mixture was decomposed in the usual manner and the product extracted with ether. Crystals separated from the brownish oil in about 24 hours. These were recrystallized from petroleum ether and benzene.

A second, and more satisfactory method for the preparation of acetophenonepinacol was by sunlight reduction of acetophenone. The procedure followed was similar to that used by Bachmann in the preparation of benzopinacol (127). In a pyrex 1-liter flask were placed 90 g. of acetophenone* and 850 cc. of isopropyl alcohol; one drop of glacial acetic acid was usually added to neutralize any basic impurities. The flask was stoppered with a rubber stopper containing a glass tube that almost reached to the bottom of the flask. The other end of the tube was drawn to a capillary. This tube was necessary in order to allow the pressure in the flask to remain atmospheric in spite of temperature changes. The flask was placed upside-down in the sun for four months in the summer. A longer period was required in the winter. After exposure, the volatile solvents were distilled off under reduced pressure. A yellow oil remained, from which crystals of acetophenonepinacol slowly formed. They were recrystallized as before. Yield 66%.

The oil which remained would not form an oxime or semicarbazone. It was not attacked by sodium hypobromite, but reacted with bromine, with evolution of hydrogen bromide, to form a brown oil.

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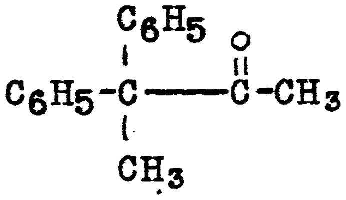
* A gift from Compagnie Parento, Ltd.

Preparation of the Diene

The first dehydration reaction which was carried out was that with acetic anhydride, which had already been described by Thörner and Zincke (109) and by Johlin (110). The pinacol (IV) was treated with acetic anhydride in a sealed tube after which any diene produced was removed from the neutralized reaction mixture by steam distillation. This method only yielded the diene occasionally and the yields were always low; on the whole the reaction was very unreliable.

The most frequent product of the above steam distillation was a ketone (VII) melting at 42-43°. This ketone formed an oxime; m.p. 149°. It seems probable that this is the pinacolone,



$$C_6H_5-\overset{\overset{C_6H_5}{|}}{\underset{\underset{CH_3}{|}}{C}}——\overset{\overset{O}{\|}}{C}-CH_3$$

described as melting at 40-41° and forming an oxime, m.p. 151° (120). However, while the pinacolone has been reported to give α,α-diphenylpropionic acid in the haloform reaction (121), this substance was unchanged by sodium hypobromite and by sodium hypoiodite. It could not be brominated by bromine in glacial acetic acid at room temperature. It crystallized very readily on steam distillation and was very easily recrystallized from dilute alcohol. This is in marked contrast to 2,3-diphenylbutadiene which added bromine readily, but which crystallized very slowly from the steam distillation product, and which was comparatively difficult to recrystallize, as Thörner and Zincke noted (109).

The ketone (VII) was always accompanied by an oil, which, when first produced was colourless and had a strong odour resembling acetophenone; on standing the colour changed to a bright yellow. No acetophenone could be detected in the oil, however, while bromination indicated that it contained some 2,3-diphenylbutadiene. Parry (122) mentioned an oil accompanying the pinacolone which turned yellow and which also possessed an odour like acetophenone.

A large amount of gummy polymer was always formed during the dehydration in the sealed tube. This remained behind during steam distillation, and hardened to a dark wax-like substance which softened about 40°. Vacuum distillation of the polymer yielded acetophenone and an oil which added bromine to form a dibromide melting at 149-151°, like the dibromide of trans-dimethylstilbene (Xb), this dibromide reacted with alcoholic potash to give a compound melting over a range 73-85°.

The addition of antioxidants to the dehydration reaction mixture hindered polymer formation and inhibited the production of the ketone. Phenyl-β-naphthylamine and copper acetate were added to the reaction mixture before dehydration, and the product, on steam distillation, was a colourless oil which, on chilling, formed crystals whose properties agreed in every way with those described for 2,3-diphenylbutadiene; the melting point was 47-48°. Thus, by adding these antioxidants, the sealed tube reaction gave fairly reproducible results, and yielded about 30% 2,3-diphenylbutadiene. As steam distillation proceeded, the oil which came over failed to solidify. It still contained the diene however, since, like the oil accompanying the ketone, it could be easily brominated. The dibromide formed (VIII) was identified with that obtained by brominating crystalline 2,3-diphenylbutadiene.

In an attempt to use up the diene as soon as it was formed, and so avoid loss through polymerization, maleic anhydride was added to the reaction mixture before dehydration in the sealed tube. No antioxidants were used with this reaction; a small amount of 4,5-diphenyltetrahydrophthalic acid (I) was obtained, but the main product was the ketone (VII). The pinacol was not dehydrated by maleic anhydride alone at 200°, but was slowly dehydrated at room temperature, in a solution of maleic anhydride in acetic anhydride. After four months, about 20% 4,5-diphenyltetrahydrophthalic acid (I) was obtained.

Acetophenonepinacol (IV), when treated with chloroacetic anhydride at 180°, was not dehydrated to 2,3-diphenylbutadiene (V), but underwent a rearrangement to form the same ketone (VII) as was encountered before.

2,3-Diphenylbutadiene polymerized to a yellow greasy substance in a few days, unless it was kept in the dark under nitrogen, in which case it was stable for two or three weeks.

The Ketone (VII), m.p. 42-43°.

Acetophenonepinacol (IV) was dehydrated by heating 10 g. of the pinacol with 27 cc. of acetic anhydride in a sealed tube at 180-200° for three hours. The reaction product was a brown liquid, which was separated from any polymer formed, made alkaline with sodium carbonate and steam distilled. The oil which came over was clear but quickly became yellow, it was shown to contain a small amount of the diene by bromination to the dibromide (VIII). The odour of acetophenone was detected but no 2,4-dinitrophenylhydrazone (129) could be prepared. The sodium nitroprusside test did not indicate acetophenone; in alkaline solution, a stable bright yellow colour was formed, which disappeared, leaving a cloudy solution, when a drop of acetic acid was added. Sometimes the ketone would crystallize out of the oil at once, or it might take some days. The yield of oil (before crystallization) was about 2 g. The crystals were recrystallized several times from methyl alcohol, after which they melted at 42-43°. They formed an oxime, m.p. 149°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.7; H, 7.1. Found: C, 86.6; H, 7.2.

The same reaction was also carried out in an autoclave, but the yield was lower. In order to prevent the walls of the autoclave from being attacked by the acetic acid which was formed during the reaction, the reagents were contained in a stoppered bottle, which was placed in the autoclave with some cellosolve, which had only a slightly higher vapour pressure than the acetic anhydride under the reaction conditions.

Chloroacetic anhydride was also used as a dehydrating agent: 44 cc. of acetic anhydride and 38 g. of chloroacetic acid were refluxed for 2 hours and the excess acetic anhydride was distilled off. The residue was used to dehydrate the pinacol by heating at 180° and atmospheric pressure. The product of this dehydration, however, was almost all crystalline ketone (VII).

The ketone would not add bromine, maleic anhydride, or sulphur dioxide in ether solution.

<u>2,3-Diphenylbutadiene</u> (V).

2,3-Diphenylbutadiene was prepared most easily, and in the largest quantities, by adding 18 cc. of acetyl bromide to 6 g. of acetophenonepinacol containing a trace of antioxidant (phenyl-β-naphthylamine). When the vigorous reaction was over, the solution was warmed on a water bath to remove excess acetyl bromide. The cold reaction mixture was then cautiously made alkaline with sodium carbonate solution. The greasy precipitate (VI), m.p. 69-73°, was filtered and dissolved in hot dilute alcohol. On cooling the diene (V) crystallized. M.p. 45-47°. Yield 30%. Bromination of the remaining oils yielded a further amount of the 1,4-dibromide (VII).

A sealed tube containing 20 g. acetophenonepinacol (IV), 54 cc. of acetic anhydride, 1 g. phenyl-β-naphthylamine and two crystals of copper acetate was heated at 180-200° for three hours. The reaction product was poured into water, made alkaline and steam distilled. The receiving flask was chilled in an ice bath and 4.6 g. solid hydrocarbon was obtained, m.p. 47-48°. Later 6 g. of an oil came over which yielded 2 g. of dibromide (VIII) on bromination. The total yield of diene was 34%. A resin (7 g.) would not steam distill, this resin adhered very firmly to aluminium.

When acetyl chloride was used for dehydration instead of acetyl bromide, the pinacol would only dissolve on warming, and there was no sign of an immediate reaction. Most of the acetyl chloride was recovered unchanged, and the residual oil, when worked up as before, yielded no crystalline product. This agrees with Zincke's observations (109).

Addition Reactions

Attempted reduction with sodium amalgam.

An alcoholic solution of 1,3 g. of 2,3-diphenylbutadiene (V) was treated with 5 g. of 3% sodium amalgam and left to stand at room temperature for 24 hours, after which it was refluxed for 5 hours. On evaporation of the solvent and removal of sodium hydroxide by filtration, the diene was recovered unchanged.

Reduction with sodium in liquid ammonia.

2,3-Diphenylbutadiene (0.3 g.) was dissolved in a mixture of 40 cc. of ether and 30 cc. of liquid ammonia. To this solution was added 0.5 g. of sodium dissolved in 30 cc. of liquid ammonia. The sodium solution was added very slowly; on stirring a gas was evolved, the deep blue colour got lighter, and a liquid tended to separate out. The solution was evaporated at room temperature with intermittent stirring. The blue colour disappeared suddenly, leaving a slight whitish precipitate in a pale green solution. Complete evaporation of the solvents left a jelly-like mass, which was boiled with alcohol, setting free considerable ether. Sodium hydroxide was filtered from the hot solution which was then evaporated to dryness. The residue was boiled with methyl alcohol, and more insoluble

alkali filtered from the hot solution. On cooling crystals formed, which, when recrystallized from dilute acetone, formed needles which melted at 169°. This compound, when dissolved in carbon tetrachloride, would not decolourize bromine. It was thought to be a bimolecular product.
Anal. Calcd. for $C_{32}H_{34}$: C, 91.9; H, 8.13. Found C, 91.9; H, 8.4.

The remaining solution yielded a solid, which on recrystallization from dilute methyl alcohol, formed crystals of meso-2,3-diphenylbutane. M.P. 116-119 °; mixed melting point with authentic meso-2,3-diphenylbutane (IX) 115-117°.

Catalytic reduction with excess hydrogen was carried out using .75 g. diene in 70 cc. of ethyl alcohol and .2 g. catalyst ($PtO_2.H_2O$) (128). The pressure fell 0.7 units in the first two minutes, then remained constant. After 2-1/2 hours the shaking was stopped and the catalyst filtered off. On evaporation of the alcohol, crystals (plates) appeared;
Anal. Calcd. for $C_{16}H_{18}$: C, 91.9; H, 8.1. Found: C,91.4; H,8.6%.
This melting point was raised when the crystals were mixed with some 2,3-diphenylbutane (IX), m.p. 119°, made by the Wurtz reaction (123). Yield 55%. The remaining oil would not crystallize.

Catalytic hydrogenation with one equivalent of hydrogen was carried out at 23°C. and 759 mm. using .18 g. catalyst ($PtO_2.H_2O$)

in alcohol, which required 40.8 cc. of hydrogen for its reduction to platinum, (calculated 36 cc.). Then .70 g. diene was added and 85.1 cc. of hydrogen was used up in 2 minutes, (1 equivalent is 83 cc.). The product was worked up as before, and the only crystalline solid recovered was .3 g. unchanged diene. The yellow oil remaining was insoluble in methyl alcohol, and had a strong anise-like odour.

<u>2,3-Diphenylbutane</u> (IX).

α-Bromoethylbenzene was prepared by treating 10 g. of phenylmethylcarbinyl acetate* with excess hydrogen bromide dissolved in glacial acetic acid. After standing 12 hours fumes of hydrogen bromide were still present, and the solution was poured into water; the oily layer was separated and dried with calcium chloride. It was then dissolved in acetone and treated with zinc dust. A vigorous reaction took place, after which the zinc was filtered and the solvent evaporated. Crystals of 2,3-diphenylbutane slowly separated from the remaining oil; they melted at 119° and were probably a mixture of the meso- and d,l- isomers. Recrystallization from dilute alcohol raised the melting point to 122°. Yield 1g.or 26%.

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* A gift from Compagnie Parento, Ltd.

2,3-Diphenyl-1,4-dibromobutene-2 (VIII), m.p. 145-7°.

A chloroform solution of 2,3-diphenylbutadiene was treated with bromine in chloroform until the colour of bromine was no longer removed on shaking. Heat was evolved, and, towards the end of the addition of the bromine solution, fumes of hydrogen bromide were given off. The solvent was evaporated and the product recrystallized from acetone. It formed long prisms, m.p. 145-7° with decomposition. It could be recrystallized from alcohol without appreciable decomposition. Other solvents used for the bromination reaction were glacial acetic acid and carbon disulphide.

Anal. Calcd. for $C_{16}H_{14}Br_2$: C, 52.5; H, 3.85; Br, 43.7.
Found: C, 52.5; H, 3.82; Br, 43.9.

The dibromide was dissolved in hot acetone and refluxed with excess zinc for two hours. The zinc was filtered, and, on cooling, 2,3-diphenylbutadiene crystallized almost quantitatively.

An alcoholic solution of the dibromide reacted with alcoholic silver nitrate to form an immediate precipitate of silver bromide. In warm acetone, permanganate was only very slowly decolorized by the dibromide, while in acetic acid solution it liberated iodine from potassium iodide very slowly. It readily dissolved in cold acetyl bromide, and was recovered unchanged when the solvent was distilled.

The 2,3-diphenyl-2,3-dibromobutanes (XIIa and XIIb).

A. Beschke's Method (111).

Trans-2,3-diphenylbutene-1,4-dicarboxylic acid* (1.0 g.) was dissolved in dilute potassium hydroxide solution. Bromine water was added until the white turbid liquid became coloured by bromine. The mixture was heated to boiling: on cooling, the tarry precipitate was filtered and recrystallized from glacial acetic acid, m.p. 146-152°, and from acetone, m.p. 142-4°; gas bubbles were given off at 144°. A mixed melting point with the dibromide (VIII) from the diene was depressed to 139-141°. Treatment of the dibromide (XII) with zinc in acetone yielded an oil. In one instance only were crystals obtained, but they melted when they touched the filter paper.

B. Lévy's Method (112,114).

Both the cis and trans isomers (Xa and Xb) of 2,3-diphenylbutene-2 (dimethylstilbene) were prepared and brominated.

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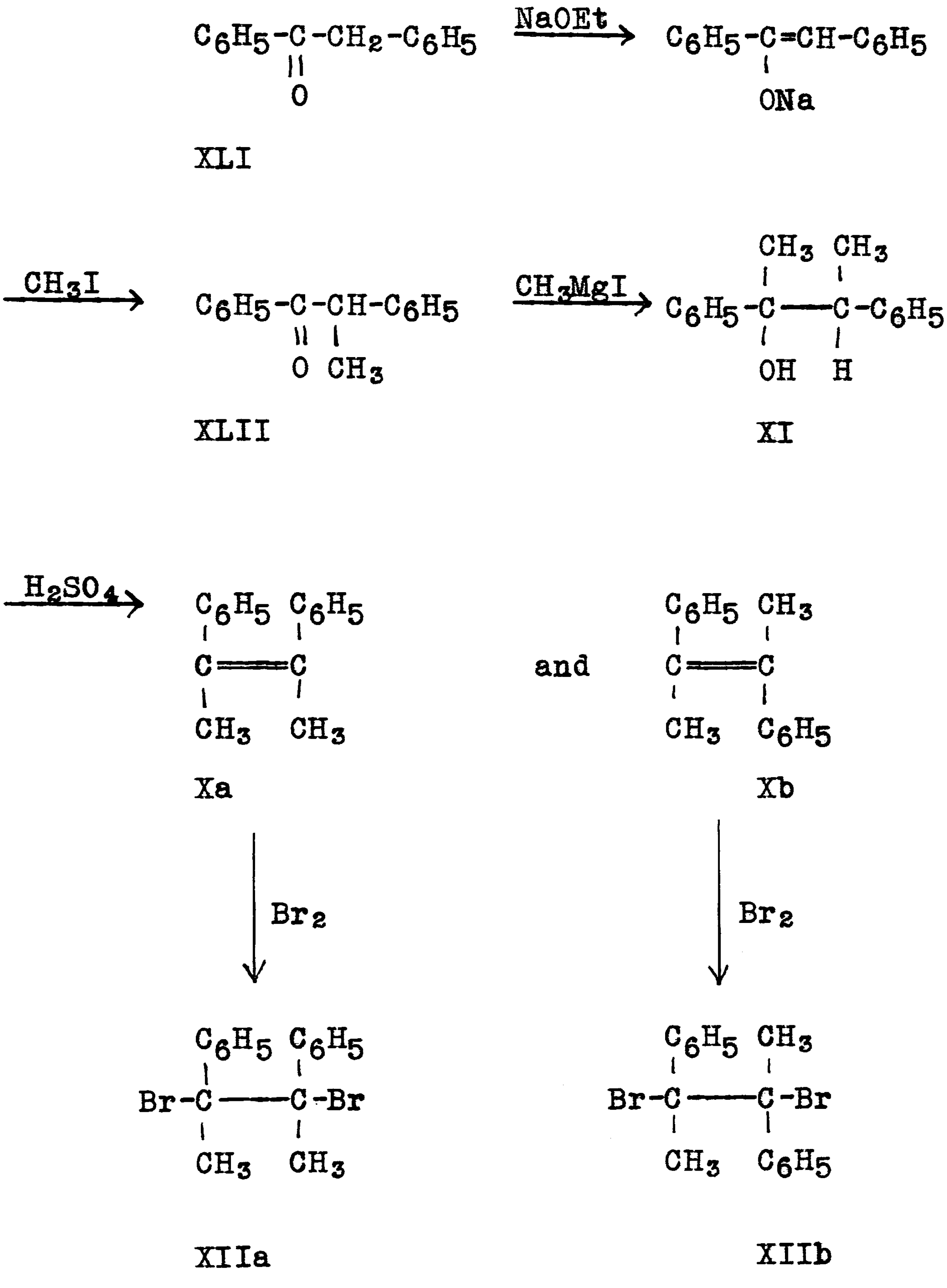
* Kindly prepared by Mr. H. B. Yuen.



α-Methyldesoxybenzoin (XLII) (147).

Sodium (1.2 g.) was dissolved in 12 cc. of absolute alcohol and 10 g. of finely powdered desoxybenzoin (XLI) was added. The mixture was heated on a steam bath for a few minutes to obtain a clear red-brown solution. To this was added 7.1 g. of methyl iodide and the mixture was heated on the steam bath for 15 minutes. Excess methyl iodide and alcohol was evaporated; then the residue was extracted with ether, dried over calcium chloride and distilled under reduced pressure to yield a product which solidified in the cold. This was recrystallized from alcohol, m.p. 45-8°, mixed melting point with desoxybenzoin (XLI) 35-40°. Yield 8 g.

2,3-Diphenylbutanol-2 (XI) (112).

An ethereal solution of methyl magnesium iodide was prepared from 32 g. of methyl iodide, 4 g. of magnesium and 150 cc. of dry ether; to this was added 28 g. of methyldesoxybenzoin (XLII). The product was worked up in the usual manner and the alcohol was distilled. B.p. 183-185° at 18-20 mm. Yield 25.5 g.

Dimethylstilbenes (Xa and Xb).

The 25 g. of 2,3-diphenylbutanol-2 (XI) was distilled under 5 mm. pressure with 5 drops of concentrated sulphuric acid. On cooling the distillate, a solid separated and was filtered from the oil. Repeated crystallizations from methyl alcohol and hexane separated the product into two fractions; the more insoluble trans-2,3-diphenyl-2,3-dibromobutane (Xb), m.p. 102-104°, and the less insoluble cis isomer (Xa), m.p. 62-64°.

Bromination of trans-dimethylstilbene (Xb).

A solution of 1 g. of the dimethylstilbene in 10 cc. of chloroform was cooled with ice and 1.6 g. of bromine in 10 cc. of chloroform was slowly added. After standing, the solvent was evaporated and the product (XIIb) was crystallized from hexane (in which it was very insoluble). It separated in long needles, m.p. 149-152°. Yield 1.2 g.

Bromination of cis. dimethylstilbene (Xa).

The cis-dimethylstilbene (1 g.) was brominated as above. The product (XIIa) crystallized in diamond shaped prisms m.p. 130-138° with decomposition. When mixed with the dibromide from the trans form (XIIb), the melting point was depressed to 120-127°.

Both dibromides when boiled with ethyl alcohol gave only very soluble oils on evaporation of the solvent. The dibromide (XIIb), from the trans-stilbene, when boiled with alcoholic potash, yielded a product which melted over a range, 73-85°.

Removal of Bromine from the Dibromides (XIIa and XIIb).

A solution of 0.5 g. of the dibromide (XIIb), from the trans-dimethylstilbene, in 10 cc. of acetone was refluxed with 3 g. of zinc dust for 1/2 hour. The solution was filtered and evaporation of the solvent yielded a crystalline residue, m.p. 43.5-50°. Recrystallization from methyl alcohol raised the melting point to 52-54°. This melting point showed no depression when mixed with cis-dimethylstilbene (Xa).

The dibromide (XIIa) from the cis-dimethylstilbene was treated as above. The crude product obtained melted at 58-61°. A mixture of this and cis-dimethylstilbene (Xa) melted at 61-62°.

Stobbe's dibromide (113).

Acetophenonepinacol (IV), (4 g.) was treated with 20 g. of acetyl bromide, in which it dissolved with evolution of hydrogen bromide. The solution became very hot. On cooling, 16 g. of phosphorus pentabromide was added; a slow reaction took place over a period of about 2-1/2 hours, when all the phosphorus pentabromide had dissolved. The solution stood over night and was then poured into a solution of sodium carbonate; the oil was extracted with chloroform. After evaporating the solvent, the dibromide was crystallized from methyl alcohol, and recrystallized from acetone: m.p. 145-147° with decomposition. A mixed melting point with the dibromide (VIII) from the diene was depressed very slightly, while one with Beschke's dibromide was depressed to 138-142°.

The preparation just outlined was repeated, replacing the phosphorus pentabromide by 1 g. of bromine, which was added very slowly to the chilled solution; this was then slowly warmed until it was refluxing. It was cooled again and made alkaline with sodium carbonate solution. The solid dibromide which separated was recrystallized from acetone, m.p. 144-146°. A mixed melting point with the dibromide (VIII) from the diene was depressed very slightly.

An acetone solution of this dibromide was refluxed with zinc dust for one hour and left to stand for 16 hours. The solution was then warmed and filtered; the solid diene was obtained on evaporation of the filtrate, m.p. 46-48°.

Ozonolysis of the dibromide (VIII).

The dibromide (2 g.) was ozonized in carbon tetrachloride solution for three hours at 0°. The ozonide was decomposed with cold water, and a solid (.2g.) was obtained which was a lachrymator; m.p. 44-7°, and mixed melting point with a sample of ω-bromoacetophenone, 44-9°. The bulk of the product was an oil from which no known compound could be isolated. It did not yield a sharply melting 2,4-dinitrophenylhydrazone (129,130). Formaldehyde could not be detected by this method nor by the formation of a dimedon or ammonia derivative; the resorcinol colour test was negative (131).

The Monobromide (VI), m.p. 78°

When a chloroform solution of 2,3-diphenylbutadiene was treated with dry hydrogen bromide, crystals of an addition product separated on evaporation.

This compound, however, was more conveniently prepared from acetophenonepinacol (IV), by treatment with acetylbromide. A quantitative yield was obtained of a crude product melting at 69-73° (page 81). This was recrystallized several times from Skelly Solve C, care being taken not to heat the solution more than was necessary, as the addition compound is easily decomposed. The residual oil from these crystallizations was brominated and the dibromide (VIII) was formed, showing that the diene was present in the oil. The addition product (VI) crystallized in prisms which melted at 78°, but after standing for a few days, yellowish oil began to appear, and the melting point was lowered to 65-69°.

An alcoholic solution of this compound reacted with alcoholic silver nitrate to give silver bromide. Quantitative determination of the silver bromide showed that the addition compound (VI) was a monobromide.

Anal. Calcd. for $C_{16}H_{15}Br$: Br,27.9. Found: Br,27.9.

2,3-Diphenylbutadiene (V) was found to be the only product when a hot alcoholic solution of the bromide (VI) was diluted and cooled. Alcoholic potash gave an instant precipitate of potassium bromide and the oil remaining was shown to be

2,3-diphenylbutadiene by bromination to the dibromide (VIII), m.p. 145-7°.

The bromide (VI) was boiled with excess zinc in acetone for one hour. The hot solution was filtered and cooled. Crystals were obtained, which, when recrystallized from acetone, melted at 204°. This was probably a product of a Wurtz reaction.

Anal. Calcd. for $C_{32}H_{32}$: C,92.3; H,7.6. Calcd. for $C_{32}H_{30}$: C,92.7; H,7.3. Found: C,92.9; H,7.5.

The acetone solution, on evaporation of the solvent, yielded an oil, which added bromine in carbon tetrachloride to form another oil from which a few crystals melting at 138-151° separated.

In the course of one experiment the bromide (VI) was treated with phenylacetylene. A crystalline solid was obtained which proved to be identical with the 2,3-diphenylbutane (IX) that was synthesised by catalytic hydrogenation of the diene (page 83).

The bromide (VI) was relatively stable to hot aqueous sodium carbonate, or sodium hydroxide, probably owing to its insolubility. It decomposed slowly on standing in the air, but was unchanged by boiling acetyl bromide.

The Diene Synthesis

4,5-Diphenyltetrahydrophthalic acid (I).

This was formed by heating 1 g. of the diene with a slight excess of maleic anhydride. After an hour on a steam bath, aqueous alkali was added, and the unreacted oil separated. On pouring into concentrated hydrochloric acid, an acid, insoluble in water, but soluble in ether, was precipitated; it was recrystallized several times from dilute alcohol and dilute acetic acid, m.p. 172-3°. Yield 66%, based on acetophenonepinacol (IV) as starting material. On further evaporation and cooling the aqueous solution gave another acid, insoluble in ether; it was recrystallized from water, melted at 118°, then gave off gas at 121° and resolidified to give a new solid which melted at 224°. The nature of this compound is unknown.

This substance, m.p. 165-170°, was also obtained, in smaller yields, by adding excess maleic anhydride to the sealed tube reaction used in the preparation of 2,3-diphenylbutadiene. No antioxidants were used. The main product of this reaction, however, was the ketone, m.p. 42-43°. The silver salt of the acid was formed and analysed for silver.

Anal. Calcd. for $C_{20}H_{16}O_4Ag_2$: Ag, 40.3. Found: Ag, 40.4

Calcd. for $C_{20}H_{18}O_4$: C, 74.5; H, 5.63. Found: C, 73.5; H, 5.98

When 6 g. of acetophenonepinacol (IV), 11 g. of maleic anhydride and 16 cc. of acetic anhydride were left in a bottle at room temperature for four months, 4,5-diphenyltetrahydrophthalic acid was formed in about 20% yield. Maleic anhydride alone at 200° did not dehydrate the pinacol.

Attempted decarboxylation reactions.

This acid (I) was recovered unchanged when treated with copper powder in boiling quinoline for several hours. Only tarry products could be isolated when the acid was distilled with zinc dust or when its sodium salt was heated with soda lime.

The acid (3.5 g.) was dissolved in an aqueous solution of 1 g. of sodium hydroxide. Excess lime (2 g.) was added and the solution was boiled for 1/2 hour. The white precipitate was filtered and the clear filtrate was evaporated to dryness. The white solid obtained on evaporation was mixed with the filtered precipitate and the mixture was dried for three days in a vacuum desiccator, before being ground up with 10 g. of lime and 7.5 g. of zinc dust to form a fine grey powder (99). Distillation of a portion of this mixture yielded a few drops of a yellow oil, and a gas, which could be ignited (yellow flame). No o-diphenylbenzene (III) could be obtained by seeding, and the oil was soluble in cold methyl alcohol, whereas o-diphenylbenzene is not.

The acid (I), (1.1 g.) was dissolved in a solution of 1.5 g. of potassium hydroxide in 8 cc. of water. To this was added a solution of 2.6 g. of potassium ferricyanide in 8 cc. of water. The mixture was heated on a steam bath for 2-1/2 hours (126). On cooling, crystals appeared which were dissolved in more water. The yellow sediment was removed by filtration, and on addition of hydrochloric acid a white to greenish precipitate came down (0.5 g.). This was recrystallized from methyl alcohol and melted at 208-212°. A mixed melting point with 4,5-diphenylphthalic acid (II) was depressed to 187-190°. Repetition of this procedure, however, always led to the recovery of unchanged 4,5-diphenyltetrahydrophthalic acid (I). The acid melting at 208-212° was fused with resorcinol and sulphuric acid, but only a very faint fluorescence was produced in the fluorescein test. Since this test, when positive, indicates two ortho-carboxyl groups (125), it seemed probable that this acid was 4,5-diphenylbenzoic acid. Adams (126) found that potassium ferricyanide removed one carboxyl group in the case of trans-9,10-dicarboxy-9,10-dihydrophenanthrene (XVI).

The Anhydride (XV) m.p. 165-170°.

When the diene synthesis with maleic anhydride and 2,3-diphenylbutadiene was carried out in xylene for three days at room temperature, a solid anhydride (XV) separated. This compound was also prepared by heating the acid (I), from the diene synthesis, just above its melting point until no more water was evolved. The liquid turned light brown and solidified on cooling; m.p. 165-170°, mixed melting point with the acid (I), 150-165°. No crystalline anhydride could be isolated when the acid was treated with acetic anhydride, or acetyl chloride.

Dyes.

The fluorescein-like dyes were made by treating 0.5 g. of the acid (I or II) with 1 g. of resorcinol and a little zinc chloride or concentrated sulphuric acid. The mixture was heated for two hours at 210°. The cold solid was broken up and dissolved in aqueous sodium hydroxide to form a fluorescein-like solution. On acidification, the dye was precipitated as the acid, filtered, and redissolved in 40 cc. of alcohol. On addition of bromine, a whitish precipitate formed but dissolved again as more bromine was added. The solution was filtered, made alkaline, and then neutralized with hydrochloric acid and filtered again. The solid dissolved in alkalis to form a red-brown dye.

4,5-Diphenylphthalic acid (II).

This acid, m.p. 205-207°, was prepared from 4,5-diphenyltetrahydrophthalic acid and 5 g. moist potassium, which were fused at 310° until no more gas was evolved. The melt was dissolved in water and extracted with benzene. On acidification of the aqueous layer crude 4,5-diphenylphthalic acid separated, m.p. 195°. Recrystallization from dilute acetic acid and dilute methyl alcohol raised the melting point to 205-207°.

Anal. Calcd. for $C_{20}H_{14}O_4$: C, 75.4; H, 4.40. Found: C,75.2; H, 5.6.

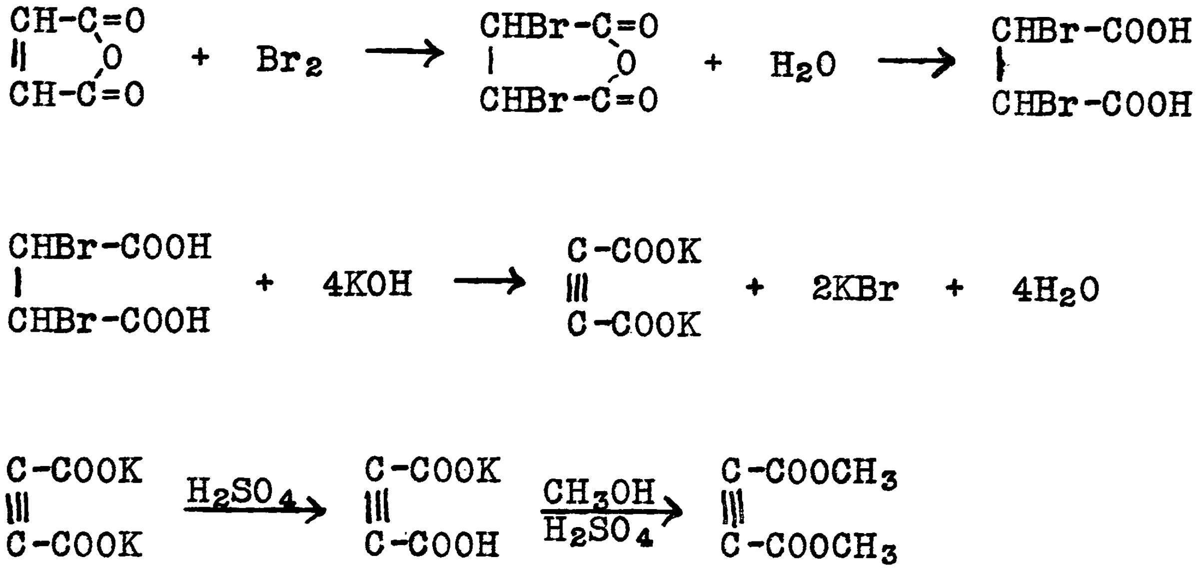
Other acids with higher melting points were sometimes obtained, depending on the conditions maintained during the fusion. Kuhn noted a similar uncertainty in melting points in the case of 3,6-diphenylphthalic acid derivatives (100). It was thought that the acid melting at 205-7° would probably be the aromatic acid - 4,5-diphenylphthalic acid (II), but some doubt was cast on this assumption by the fact that, in one instance, aluminium chloride seemed to convert the acid (II) to the one which melted at 172-3° (I). This reaction could not be repeated, however, and the acid (I) might have been present originally as an impurity due to incomplete fusion. The acid used for the aluminium chloride reaction melted at 190-95°, so was obviously impure.

The aromatic acid (II) was recovered unchanged after heating 2 g. with 1 g. of selenium for 3-1/2 hours at 325°. Fusion with sodium amide under nitrogen destroyed the acid, but yielded a chloroform soluble compound, which, when recrystallized from dilute methyl alcohol, was a tarry solid melting at 105°.

The benzene layer from the alkaline fusion reaction and the remaining solid was boiled with methyl alcohol and filtered. On cooling, crystals of o-diphenylbenzene (III) formed; a mixed melting point with Eastman o-diphenylbenzene was not depressed.

Methyl acetylenedicarboxylate (XVII), (133).

The ester was prepared as shown in the outline (127). This method was found to be superior to one involving methylation with dimethyl sulphate.



Bromine (160 g.) was added to 98 g. of maleic anhydride in 100 cc. of chloroform. After standing for 48 hours the chloroform was distilled under reduced pressure, and the remaining liquid poured upon ice. The mixture containing the dibromosuccinic acid was then poured into 2 liters of water containing 225 g. of potassium hydroxide, heated at 80° for

30 minutes, with mechanical stirring, then cooled to 12°. A solution of 103 g. of concentrated sulphuric acid in 150 cc. of water was then added, and the acid potassium salt came down on stirring. After standing over night, the salt was filtered and dried. Esterification was brought about by refluxing with 4 parts methyl alcohol and 2 parts concentrated sulphuric acid for 3 hours. The mixture was poured into water and the yellow oil washed with dilute sodium carbonate and with water, extracted with ether, and dried over calcium chloride. The ether was distilled, and the ester distilled over at 195-198° with considerable decomposition; this was avoided by distilling under reduced pressure.

<u>4,5-Diphenylphthalic acid (II)</u> was prepared by heating the acetylenedicarboxylic ester (XVII) with the oil containing 2,3-diphenylbutadiene at 180-190° until the colour deepened to a red-brown. Aqueous alkali was added and unreacted hydrocarbon removed by steam distillation. The alkaline solution was then poured into concentrated hydrochloric acid and the mixture boiled to coagulate the 4,5-diphenylphthalic acid, m.p. 192-195°; no depression of melting point when mixed with the acid (II), m.p. 195°, from the alkaline fusion of 4,5-diphenyltetrahydrophthalic acid.

<u>Diglycolic ester (XIX)</u> (134).

The acid was prepared by dissolving 910 g. of barium hydroxide octahydrate (free of barium carbonate) in 2.5 liters of water heated to 50°, and adding 272 g. of chloroacetic acid. The mixture was heated to boiling, when a vigorous reaction took place. It was boiled for one hour, cooled in an ice bath, and the barium salt of the diglycolic acid filtered. Dilute sulphuric acid was added until the solution was slightly acid to litmus, and the barium sulphate was filtered. The water was evaporated on a steam bath, leaving white crystals of diglycolic acid, m.p. 120-136°. The diethyl ester was made by treating the acid with 1500 cc. of dry ethyl alcohol saturated with dry hydrogen chloride. The mixture stood at room temperature for 36 hours, when the ethyl alcohol was distilled and the ester purified in the usual way. The ester boiled at 32-35° at 15 mm. The yield was 15%.

<u>3,4-Diphenylfuran-2,4-dicarboxylic acid (XX).</u>

This acid, m.p. 213-215°, was made by the method suggested by Hinsberg (135), who prepared only the corresponding thiophene compounds. Benzil was recrystallized, and 5 g. dissolved in 70 cc. of dry methyl alcohol with 5 g. of the diglycolic ester. To this solution was added 1 g. of sodium dissolved in 20 cc. of dry methyl alcohol, and the whole mixture was refluxed until it became almost black. Longer heating did not improve the yield. The solution was poured into water, almost all the alcohol removed by distillation, and the cold liquid was filtered and poured into concentrated hydrochloric acid to precipitate the 3,4-diphenylfuran-2,5-dicarboxylic acid. This acid gave a bright red colour when dissolved in cold concentrated sulphuric acid; on heating, this solution showed a very deep blue fluorescence.

3,4-Diphenylfuran (XVIII).

The furan, m.p. 110°, was also prepared by the method suggested by Hinsberg (135), by heating the dicarboxylic acid (XX) just above its melting point until no more gas was evolved, extracting with chloroform and recrystallizing from dilute methyl alcohol. It gave a bright yellow colour in cold concentrated sulphuric acid.

It could also be prepared by decarboxylation of the acid (XX) with copper powder in quinoline at 210°, but in this case an unidentified non-acidic compound, which crystallized from ethyl alcohol, m.p. 200-203°, was obtained as well as the 3,4-diphenylfuran. An acidic product (XXI) was always recovered, When purified by crystallization from dilute acetic acid, a solid was obtained: M.p. 221-255° with decomposition. This seems to be the monocarboxylic acid.
Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.2; H, 4.5. Found: C, 76.5, H, 4.8.

4,5-Diphenylphthalic acid (II).

The aromatic acid was obtained in very poor yield and in an impure condition by subjecting the 3,4-diphenylfuran

(XVIII) to a Diels-Alder reaction with maleic anhydride. The two compounds were dissolved in benzene and the mixture boiled for a few minutes, then left to stand for 24 hours. A water-insoluble acid (XXII), m.p. 231-235°, was isolated. This acid gave a green fluorescent dye when fused with resorcinol and a drop of concentrated sulphuric acid, and made alkaline.

The acid was dehydrated by Johnson's method for removing endo-oxygen bridges from furan-maleic anhydride addition compounds (136). The acid was dissolved in glacial acetic acid saturated with hydrogen bromide, and left to stand over night. The mixture was then diluted, filtered, and the solid re-precipitated. It melted at 195-205° and the melting point was not depressed when it was mixed with 4,5-diphenylphthalic acid, m.p. 192-195°.

Diene synthesis with α-naphthoquinone.

The reaction was carried out by dissolving 6 g. of α-naphthoquinone in 100 cc. of xylene and adding 8 g. of 2,3-diphenylbutadiene. The mixture was refluxed for 2 hours when it had become very dark, and was then left to stand for 12 hours. The dark red-brown precipitate was removed by filtration and dissolved in ethyl alcohol to form a crimson solution. Addition of alcoholic alkali gave a brilliant blue solution which soon became greenish. This solution was oxidized by bubbling air through it for 1/2 hour; on addition of concentrated hydrochloric acid, a red-purple precipitate was formed, which was recrystallized from dilute acetic acid. M.p. 200° with decomposition to form a tar, but no evolution of gas.

Analysis. Found: C, 76.9; H, 3.7%.

Possible empirical formula; $C_{26}H_{14}O_5$: C, 76.6; H, 3.5

The xylene solution was distilled, and the remaining tar was extracted with boiling acetone. An insoluble residue remained which resembled the polymerized diene. A light-coloured crystalline solid was obtained from the acetone, and was recrystallized several times from glacial acetic acid to give a yellow compound (XXIV), m.p. 205-206°.

Anal. Calcd. for $C_{26}H_{18}O_2$: C,86.2; H,4.97. Found: C,87.1; H,4.4.

This yellow quinone (XXIV) dissolved in cold concentrated sulphuric acid to give a brown solution. Dilution of this solution gave a yellow solid, which was shown by mixed melting points to be the original quinone. When treated with sodium hydrosulphite in very dilute methyl alcohol, a green compound is formed which dissolves when more water is added. No oxidation was observed when air was bubbled through the solution, but sodium perborate or acidification regenerated the quinone. Zinc in sodium hydroxide solution gave a red colour with the quinone. Acidification turned the solution yellow, and the quinone was slowly regenerated by bubbling air through the acid solution for several hours.

The red compound was treated in a similar manner. It also gave a brown solution with sulphuric acid and was regenerated by dilution. It gave a yellow-brown compound with sodium hydrosulphite in dilute methyl alcohol but the original compound could not be isolated from the colloidal solution obtained on acidification and oxidation. Zinc in aqueous alkali gave a red solution from which the original solid was regenerated on acidification. The compound was fused with moist potassium hydroxide in a nickel crucible for one hour and the melt dissolved in water. The aqueous solution was extracted with chloroform and a small amount of brown tar was obtained. The aqueous layer was poured into concentrated hydrochloric acid and a small amount of tarry acid was obtained which melted over a range, 215-225°. The filtrate was extracted with ether, but only a very slight amount of yellow tar was obtained, which was insoluble in boiling water.

The red compound did not melt sharply but decomposed to form a tar, although no gas was evolved. Vacuum distillation of the red compound yielded a tarry product which did not seem to be produced at a definite temperature, but to be the result of decomposition.

Attempted diene synthesis reactions.

When the diene (V) was heated for three hours with slightly more than two equivalents of benzoquinone in methyl alcohol solution, a brown solid was formed, which was recrystallized from tetrachloroethane and Skelly Solve B. The solid obtained was light red-brown and melted over a range, 145-165°. It dissolved in aqueous sodium hydroxide to form a light brown solution, which changed to black on bubbling air through it for two hours. No precipitate formed however, even on acidification. Extraction with benzene yielded the original product.

The diene was heated with β-benzoylacrylic acid for two hours in alcohol. The only product isolated was the red polymer, m.p. 270° (146). No better results were obtained when the reaction was carried out in a sealed tube heated eight hours at 100°. A trace of hydroquinone was added as an antioxidant and no red compound was formed, but the only product was a tar.

Acetylene was prepared by dropping water on calcium carbide, and was bubbled through a solution of 0.5 g. of the diene in liquid naphthalene for about fifteen minutes. The solution was allowed to cool as slowly as possible, in contact with an atmosphere of acetylene. The mixture was dissolved in hot alcohol and a few drops of water added. An oil separated, which on recrystallization from dilute alcohol yielded 0.2 g. of the diene, but no o-diphenylbenzene (III).

Crude 2,3-diphenyl-2-bromobutene-3 (VI), m.p. 69-73°, (22 g.) was dissolved in 10 g. of phenylacetylene and heated at 100° for 8-1/2 hours, then left to stand at room temperature for four days. The mixture was distilled, but very little phenylacetylene was recovered (b.p. 143°); hydrogen-bromide was evolved. The mixture was treated with excess aqueous sodium carbonate and left to stand for 12 hours. Steam distillation yielded a pungent yellow oil and a small amount of a crystalline solid which was recrystallized from methyl alcohol, dilute ethyl alcohol and finally dilute acetic acid, which raised the melting point to 102-3°. When mixed with 2,3-diphenylbutane (IX), prepared by catalytic hydrogenation of the diene (page 83), m.p. 116-7°, the melting point was raised to 116°. The oil obtained by steam distillation was distilled under reduced pressure. A colourless liquid came over at 60° and 20 mm. At 270-280° and 20 mm., a yellow oil was obtained from which a few crystals melting at 140-155° separated. They could not be further purified.

When the same reaction was repeated using the pure diene (V) instead of the crude monobromide (VI), an oil was obtained as before, but no crystalline compound could be isolated. Similar negative results were obtained when 5 g. of the diene was heated with 1.5 g. of crude phenylbenzoyl-acetylene in xylene. The mixture was refluxed for six hours and left to stand for three days. No crystalline product could be isolated from the reaction mixture.

Miscellaneous Reactions

Sulphur dioxide.

Sulphur dioxide was bubbled through a solution of 0.5 g. of the diene in 20 cc. of ether for two hours. The solution was then placed in a sealed tube and heated for one hour at 100°. After 12 hours the tube was opened, and the solvent evaporated. The unchanged diene was recovered in crystalline form.

Friedel-Crafts Reaction.

The anhydride of 4,5-diphenylphthalic acid was prepared by refluxing 0.5 g. of the acid for 3-1/2 hours with acetic anhydride. The excess acetic anhydride was removed by distillation and the residual oil was dissolved in 4 cc. of dry benzene and poured slowly into a mixture of 1 g. of aluminium chloride in 3 cc. of dry benzene, which was cooled with an ice-salt mixture. No reaction occurred until the solution was warmed until gently refluxing. This refluxing was continued for 3/4 hour, then the reaction mixture was left to stand for 12 hours. It was decomposed in the usual manner and steam distilled to remove benzene and acetophenone. The remaining tar was boiled with sodium carbonate, filtered, and the filtrate acidified with acetic acid. Only a slight turbidity appeared. The o-benzoyl acid (XXV) m.p. 250 , if formed, should have precipitated under these conditions (103).

None of the starting material (II) was recovered.

Coupling Reaction (67,132).

A solution of 30 cc. of concentrated sulphuric acid in 10.5 cc. of water was cooled below 10°, and 1.5 g. of sodium nitrite was added. The solution was warmed gently to 70°, when it became clear, then cooled again below 10° in an ice-salt mixture. The solution was stirred mechanically while 1.8 g. of freshly recrystallized 2,4-dinitroaniline in 15 cc. of pyridine was added dropwise. The solution was stirred for 2 hours after addition was complete; 1 g. of urea was then added. A solution of 2 g. of 2,3-diphenylbutadiene in pyridine was added next; this caused the solution to turn red: after a few minutes ice was added, and finally water. The mixture stood for 12 hours, and was then extracted with chloroform. Addition of Skelly Solve C to the chloroform solution precipitated a dark red solid. The product from the first run melted at 100-110°, while that from a later run melted at 167°.

Degradation of the Polymer.

The ribbon of polymerized material (1 g.) which, was often formed during the sealed tube reaction, was distilled under reduced pressure. At 140-170° and 20 mm. an oil (0.5 g.) was collected which was shown to contain acetophenone by preparation of a 2,4-dinitrophenylhydrazone (129), m.p. 228°, mixed melting point with an authentic sample 229-231°. The remaining oil (0.3 g.) would not crystallize, but bromination in carbon tetrachloride yielded the dibromide (XIIb), m.p. 149-151°, which was formed by brominating trans-dimethylstilbene (Xb). A black tar remained in the flask after distillation.

SUMMARY

The preparations and reactions of 2,3-diphenylbutadiene have been investigated. It is most conveniently prepared from acetophenonepinacol by dehydration with acetyl bromide.

The diene has been reduced with hydrogen in the presence of a platinum catalyst; 2,3-diphenylbutane was isolated. This same butane was also formed when the diene was reduced by sodium in liquid ammonia.

Contrary to the literature, the diene readily formed a solid dibromide under the proper conditions. This compound decomposed at its melting point, and seemed to decompose slightly on standing in moist atmosphere. The diene was readily regenerated by treatment with zinc dust. Ozonization indicated that the compound was 2,3-diphenyl-1,4-dibromobutene-2. It was shown that this must be the compound prepared by Stobbe and considered by him to be 2,3-diphenyl-2,3-dibromobutane.

The two isomeric 2,3-diphenyl-2,3-dibromobutanes were synthesised in order to identify one of them with the dibromide described by Beschke.

The diene added one mole of hydrogen bromide to form the monobromide, 2,3-diphenyl-2-bromobutene-3.

In the diene synthesis 2,3-diphenylbutadiene reacted

with maleic anhydride to give 4,5-diphenyltetrahydrophthalic acid; on fusion of the latter with potassium hydroxide, 4,5-diphenylphthalic acid was produced. This aromatic acid was obtained (a) from 2,3-diphenylbutadiene and methyl acetylenedicarboxylate, and (b) by dehydration of the addition product of maleic anhydride and 3,4-diphenylfuran. o-Diphenylbenzene, arising from decarboxylation during the alkaline fusion, was also isolated; its occurrence proves the formation of a six-membered ring in the addition reactions. The diene also reacted with α-naphthoquinone to yield, on oxidation, 2,3-diphenylanthraquinone and an unidentified compound. It did not appear to react with benzoquinone, β-benzoylacrylic acid, acetylene, phenylacetylene and phenylbenzoylacetylene.

No sulphone was formed when the diene was treated with sulphur dioxide, but it coupled with diazotized 2,4-dinitroaniline in pyridine solution.

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