# REACTIONS OF TETRAHYDROLINALOOL

by

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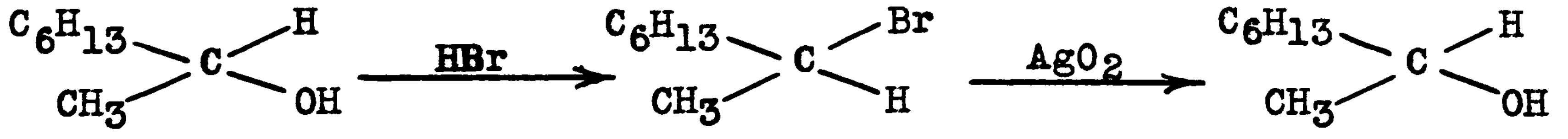
# REACTIONS OF TETRAHYDROLINALOOL

## Theoretical

### (a) Historical Introduction

Considerable work has been done on the halogenation of optically active secondary carbinols. Pickard and Kenyon (1) have prepared a number of optically active secondary halides from the corresponding carbinols. They used hydrogen halides as the halogenating agents and in every case tested the conversion was found to be accompanied by a change in sign of rotation. They produced evidence that a Walden inversion was associated with this change of sign of rotation. They also believed that no racemization had occurred. In a later paper (1a) they reported the regeneration of an optically active secondary carbinol from the halide by hydrolysis. The following changes were realized:-



d-B-octanol 1 d-B-octanol

Two complete inversions of configuration were believed to have taken place and the change from the bromide to the carbinol was also accompanied by a Walden inversion.

References: (1) Pickard R.H. and Kenyon J. J.C.S. <u>99</u>, 45, (1911)
(1a) Pickard R.H. and Kenyon J. Ber. <u>45</u> 1592 (1912)

Levene and Mikeska (2) in a study of secondary phenyl carbinols found that the two lower homologues of the series (methyl and ethyl phenyl carbinols) formed, on halogenation with hydrogen bromide a bromide having the opposite sign of rotation to the carbinol while the higher homologues under the same conditions formed bromides rotating in the same direction.

Levene and Mikeska (3) found that in the presence or absence of pyridine the action of thionyl chloride on optically active aliphatic hydroxy compounds e.g. 1 B-octanol is accompanied by a change in sign of rotation of the chloride. However, when a phenyl group is attached to the asymmetric carbon atom as in phenyl methyl carbinol Kenyon and Phillips (3a) found that a change in sign of rotation of the chloride is produced by the action of thionyl chloride in the presence of pyridine while the sign of rotation remains the same if thionyl chloride is used alone. Phosphorus trichloride in the presence or absence of pyridine was found to produce a chloride having the opposite sign of rotation to the phenyl methyl carbinol but there is less racemization when pyridine is used. In most cases of optically active secondary carbinols evidence has been advanced that a change in sign of rotation in the preparation of the halide indicates that a Walden inversion has taken place.

References: (2) Levene P.A. and Mikeska L.A. J. Biol.Chem. 70 355 (1926)
(3) Levene P.A. and Mikeska L.A. Ibid. 59,45 (1924)
(3a) Kenyon J, Phillips H, Martin, Taylor, J.C.S. 382 (1931)

A number of mechanisms have been proposed to account for Walden's inversion. Fischer (4) and Werner (4a) independently assumed addition reactions to explain the Walden inversion. Werner, furthermore, postulated simultaneous dissociation and addition. Both authors assumed that the entering group might or might not take the place of the dissociating group.

Lewis (4b) introduced the idea of the face centered bond to explain the Walden inversion. His explanation is as follows: - "Consider a carbon atom attached to the four radicals $R_1$, $R_2$, $R_3$, and $R_4$, and let us assume that a fifth group $R_5$, becomes temporarily attached to the carbon atom near to the face of the tetrahedron which is opposite to $R_1$. A slight shift of the kernel might make it now the centre of a new tetrahedron with corners at $R_2$, $R_3$, $R_4$, and $R_5$, while $R_1$ would become detached from the molecule. Then if the radical $R_5$, in the new molecule were to be replaced by the radical $R_1$, the resulting molecule would be the mirror image of the one with which we started. In this explanation it is not necessary to assume that the five radicals are attached to the carbon for any appreciable period of time, indeed it might be assumed that the $R_1$ leaves at the same instant that the $R_5$ becomes attached to the carbon atom."

References: (4) Fischer E. Ann. 381 123 (1911)

(4a) Werner A. Ber. 44 873 (1911)

(4b) Lewis G.N. "Valence and the Structure of Atoms and Molecules, P.113 Chemical Catalogue Co. (1923).

Pauling (4c) and Slater (4d) have shown by quantum mechanics that the carbon atom has a tendency to form a bond at each face of the tetrahedron. They have also shown that the stronger the bond is to the apex, the weaker the bond-forming power is to the opposite face and vice versa. In the case of a compound such as $R_1R_2R_3CCl$ the C-Cl bond is relatively weak as shown by dipole and x-ray diffraction measurements. A particle with unbonded electron pairs such as a chloride or a hydroxyl ion will therefore require a smaller energy of activation to react with $R_1R_2R_3CCl$ if it approaches the carbon face directly opposite to the chlorine. This leads to complete inversion of configuration for a reaction which takes place in one step.

Experimental evidence for the existence of face centred bonds has been advanced by Menke (4e) on the basis of x-ray diffraction measurements. Using this face centred bond theory Olson (5) concludes that every reaction of substitution by a negative group or ion is accompanied by inversion. When no inversion occurs Olson postulates a reaction taking place which involves two inversions. For example he explains the behaviour of l-phenyl chlor acetic acid in aqueous solution on this basis. McKenzie and Clough (5a) report that when l-phenyl chlor acetic acid is treated with water, l-mandelic acid results with a retention of configuration. To account for this Olson postulates three reactions taking place simultaneously.

References:
(4c) Pauling L. J. Am. Chem. Soc. 53 1367 (1931)
(4d) Slater, J.C. Phys. Rev. 37 481 (1931)
(4e) Menke H. Phys. Zeits. 33 593 (1932)
(5 ) Olson, A.R. J. Chem. Physic I, 418, (1933)
(5a) McKenzie A. and Clough, G.W. J. Chem. Soc. 95, 777 (1909)

The initial reaction as postulated by Olson is:-

$$\text{l-}C_6H_5CHClCOOH + OH' \longrightarrow \text{d-}C_6H_5CHOHCOOH + Cl' \quad (1)$$

As the concentration of chlorine ion from the above reaction increases the following reaction is said to occur:-

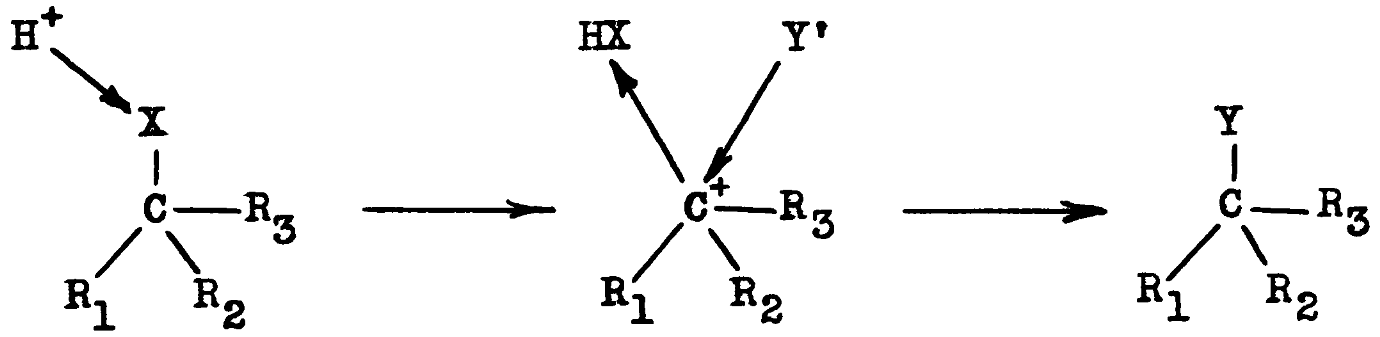
$$\text{l-}C_6H_5CHClCOOH + Cl' \longrightarrow \text{d-}C_6H_5CHClCOOH + Cl' \quad (2)$$

If reaction (2) is fast compared to reaction (1) then a racemic mixture will result. If reaction (1) is the faster then d-mandelic acid will predominate. However, the results of McKenzie and Clough (5a) show that l-mandelic acid can result from the reaction of l-phenyl chlor acetic acid and water so the above mechanism does not explain the facts. However, Olson suggested that a third reaction took place involving the face centered bond.

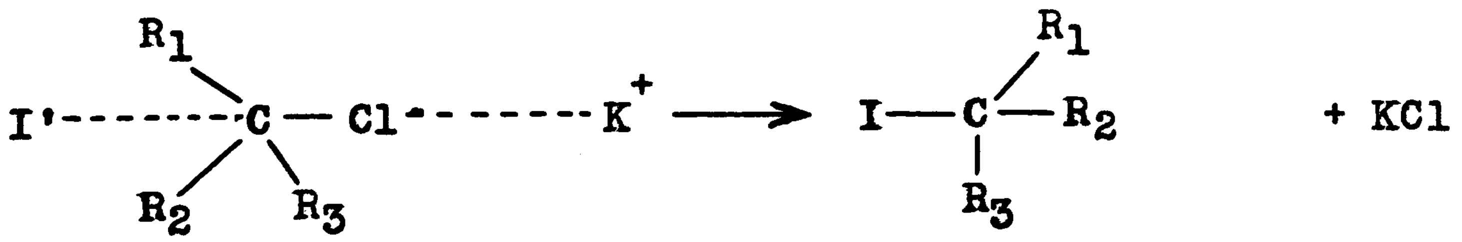
If in the l-phenyl chlor acetic acid the face of the asymmetric carbon atom opposite to the chlorine were absorbed on some surface, the carbon chlorine bond would be weakened causing the dissociation of chloride ion and inversion. Hydroxide ion could now add on where the chlorine came off again causing inversion and releasing the molecule from the surface. The net result would be the production of l-mandelic acid from l-phenyl chlor acetic acid as follows:-

$$\begin{aligned} &\text{l-}C_6H_5CHClCOOH + \text{Wall} \longrightarrow \text{d-Wall Complex} + Cl' \\ &\text{d-Wall Complex} + OH' \longrightarrow \text{l-}C_6H_5CHOHCOOH \end{aligned} \quad (3)$$

Polanyi et al (6) distinguished between substitutions affected by an anionic reagent (negative mechanism) and those in which the attack is by a cation (positive mechanism). They based their conclusions on the observation of the reactivities of primary, secondary and tertiary halides toward sodium vapour, on the one hand, and toward sodium iodide, on the other. The order of reactivity was the reverse in the second case. The authors then postulated that substitution with positive ions took place on the side of the halogen, and so proceeded without inversion. The following reaction illustrates this point:-



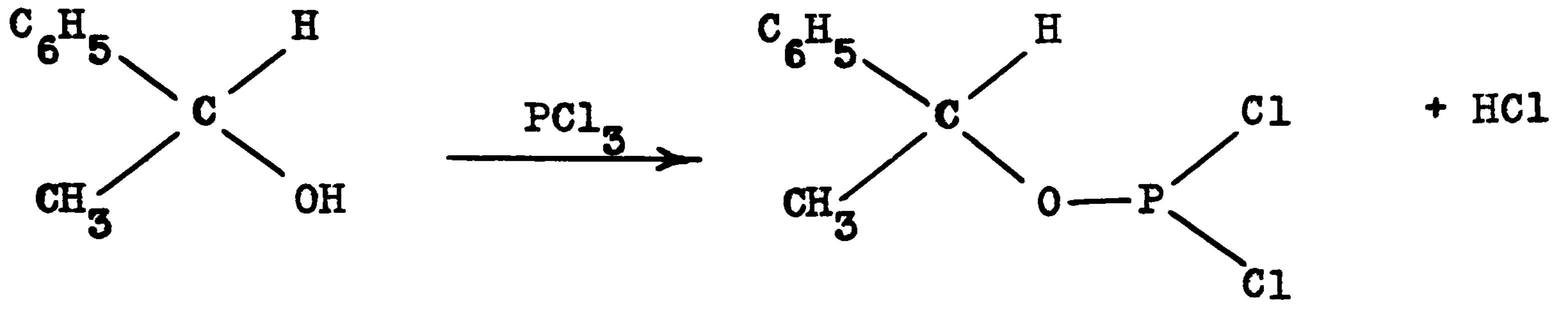
Substitution with a negative ion was postulated as taking place on the opposite side of the halogen and hence always resulted in a Walden inversion. The following diagram illustrates this mechanism:-



References: (6) Meer N. and Polanyi M., Z. Physik. Chem. Abt. B. 19, 164, (1932)

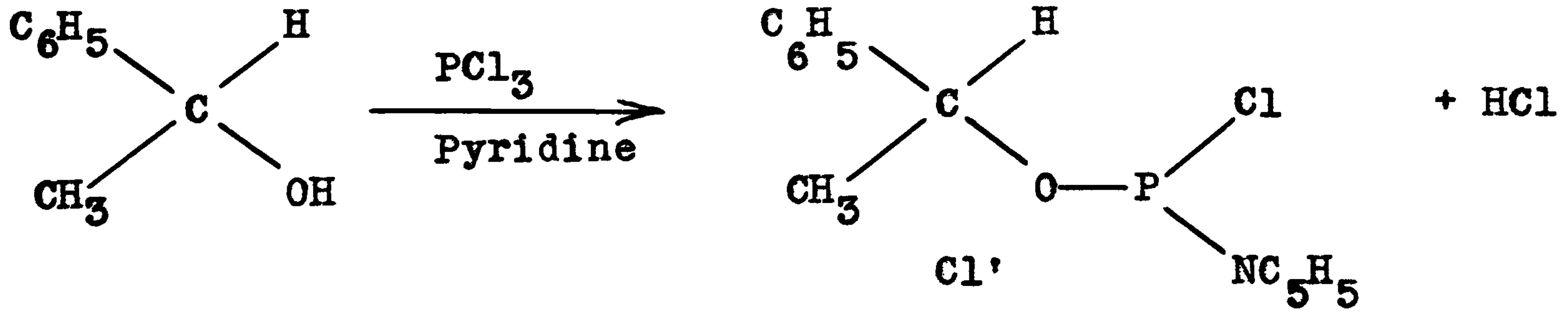
Bergmann E., Polanyi M., and Szabo A.L. Tr. Faraday Soc. 32, 843 (1936)

Kenyon and Phillips (3a) explain the action of thionyl chloride and phosphorus trichloride on secondary phenyl carbinols by the assumption of an addition compound. e.g.



The C-O bond then breaks and leaves the asymmetric carbon atom fragment charged positively. This fragment attracts the negatively charged chlorine ion in such a way as to produce retention or inversion.

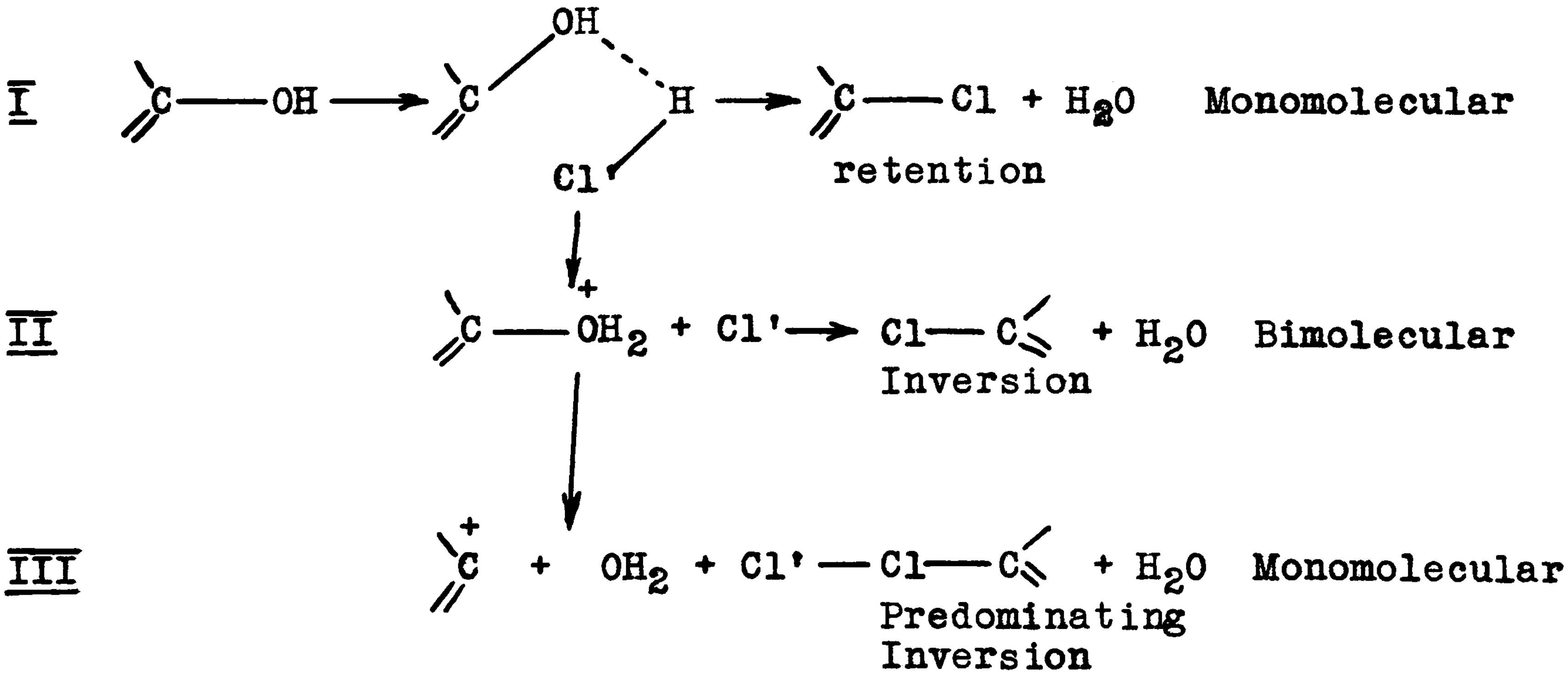
They explain the action of pyridine in aiding inversion by the following reaction:



The pyridine displaces as a chlorine ion a chlorine atom covalently linked to the phosphorus atom. The pyridine now linked to the phosphorus creates an additional positive centre in the group about to leave the molecule. This weakens the linkage between the asymmetric carbon atom and the group and at the same time enables this group when it breaks away to take with it the bonding electrons from the octet of the asymmetric carbon atom. This carbon atom is thus left positively charged and in a condition in which it can combine with a negative ion in a manner likely to lead to an inversion.

None of the above mechanisms permit of any accurate predictions to be made as to whether or not an inversion will take place. For example they do not explain the behaviour of the homologous series as reported by Levene and Mikeska (2) wherein the first two carbinols give inversion with hydrogen halide while the higher members of the series do not.

Hughes, Ingold et al (7) assume the formation of an intermediate of this type and postulate three mechanisms by which it may break down. For example in the halogenation of secondary carbinols with hydrogen chloride they postulate the following reactions as being possible



From their work on the kinetics of the above replacement reaction they conclude that since negative mechanism substitutions

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Reference: (7) Cowdrey W.A., Hughes E.D., Ingold C.K., Masterman S. and Scott A.D. J. Chem. Soc. 1252 (1937) are always nucleophilic and bimolecular all such reactions must lead to an inversion of configuration. This conclusion agrees with that reached by Polanyi et al (6) and Olson (5).

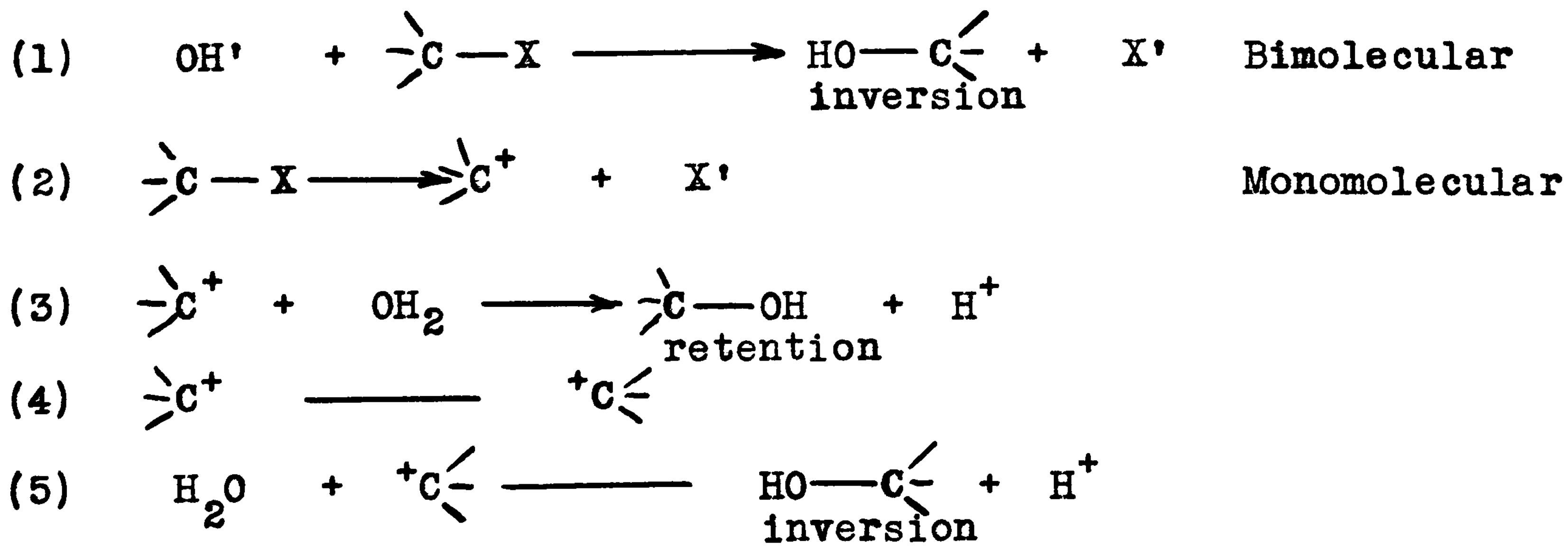
In a study of the bromination of a series of secondary phenyl carbinols with hydrogen bromide at different temperatures Levene and Rothen (8) found that for methyl, ethyl and propyl phenyl carbinols the reaction proceeded predominately without inversion at temperatures below -36°C. When the reaction was carried out at -80°C. no inversion occurred and a white crystalline solid was found to separate out. This was assumed to be an addition compound probably of the same structure as that postulated by Ingold (Reaction I above). Levene and Rothen (8) found evidence for two different mechanisms for substitution with retention of configuration and another mechanism for substitution with inversion. This was contrary to Ingold's postulations which included only one mechanism for a reaction proceeding with retention of configuration. The effect of temperature did not appear when the above reaction of substitution was carried out in a solvent (aliphatic carbinols, diethyl ether, and benzene being used) and in these solvents inversion of configuration was observed even at low temperatures.

As a consequence of this work, Ingold's statement: - that replacement by inversion of the OH group of all aliphatic and simple aromatic carbinols is the rule - must be restricted

Reference: (8) Levene P.A. and Rothen A. J. Biol. Chem. 127, 237 (1939) to the saturated aliphatic secondary carbinols. Whether a retention or inversion of configuration takes place in the preparation of halides from the simple aromatic carbinols depends on the thermodynamic environment in which the reaction is carried out. The simple aliphatic secondary carbinols could not be tested out in this respect since they would not react at very low temperatures even with hydrogen iodide.

Recently Winstein and Lucas (9) found that the reaction between hydrogen bromide and the 3-bromo-2-butanols at room temperature produced the corresponding bromide with complete retention of configuration. This represents another exception to Ingold's rule and shows that the structure of a compound as well as the thermodynamic environment may influence the mode of replacement of one group by another.

For the replacement of the halogen of alkyl halides by an OH group (hydrolysis) Ingold *et al* (10) postulated the possibility of the following reactions taking place:-



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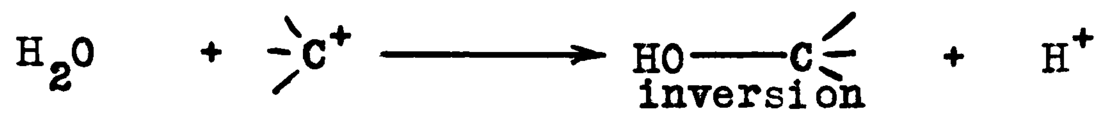
References: (9) Winstein S. and Lucas H.J. J. Am. Chem. Soc. 61 1576 (1939)

(10) Hughes E.D., Ingold C.K., Masterman S., Scott A. J. Chem. Soc. 1196-1208 (1937)

Another possible reaction which leads to the same result as (5) and omits step (4) is shown as follows:-

(6) 

Reaction (1) above is bimolecular and would lead to complete inversion of configuration just as in the replacement of OH by Cl. Reactions (2) to (5) and (6) are said to occur simultaneously but reaction (2) is the governing reaction being slower than the others and in effect the hydrolysis would be measured as a monomolecular reaction.

They postulate that this unimolecular substitution would cause inversion of configuration with considerable accompanying racemization - that is reaction (5) or (6) above would predominate. From an actual study of the kinetics of hydrolysis of optically active B-octyl chloride or bromide and $\alpha$ -phenyl-ethyl halides they conclude that all such solvolytic reactions are monomolecular and the conversion to the corresponding alcohol is accompanied by inversion of configuration and racemization. They explain the predominance of inversion (reaction (5) and (6) above) over retention of configuration (reaction (3)) by the argument that usually X' will shield the ion $>C^+$ sufficiently so that the reaction occurs more easily at the side away from X' than at the side toward X' so that inversion predominates. Also X' shields the $>C^+$ ion so that the sterically unstable $>C^+$ ion will not racemize by assuming a planar configuration.

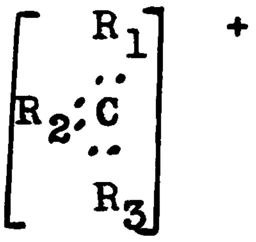
Whatever the mechanism or mechanisms, we must conclude from what is now known about secondary alcohols and halides, that replacement of the OH by X involves mainly inversion. Replacement involving retention of configuration undoubtedly may occur at the same time, giving the impression that considerable racemization may have occurred. At -78°C rentention of configuration, however, may predominate completely. There is of course also the possibility that some of the racemization may have occurred due to the free positive ion(if it exists at all) assuming a planar configuration - a type of Werner racemization - especially if the shielding of this positive ion by the negative ion is insufficient. There may also be some racemization which takes place after the halide has been formed due to a common ion effect, but this is probably very small, since Stevens et al (10a) found that B-hexanol with fuming hydrochloric acid gave a chloride after one day of $\alpha_D$ -12.58 and $\alpha_D$ of -11.52 after two weeks. This common ion effect is probably negligible.

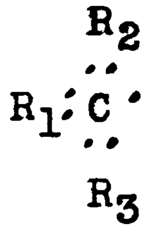
We must conclude also that replacement of X by OH probably follows the same course, with inversion predominating at ordinary temperatures.

Very little work has been done on the study of optically active tertiary carbinols. Wallis and Adams (11) succeeded in preparing d and l forms of phenyl biphenyl

Reference: (10a) Stevens P.G., Higbee W.E.,Armstrong R.T.
J. Am. Chem. Soc. 60, 2658 (1938)
(11) Wallis E.S. and Adams F.H.
J. Am. Chem. Soc. 55, 3838, (1933)

alpha-naphthyl carbinol. The optical activity of the two forms was $[\alpha]_D^{20}$ $\pm 5.6^\circ$ in carbon tetrachloride solution. The action of thionyl chloride at $-6^\circ C$ on either of the two forms resulted in a chloride which was completely racemized.

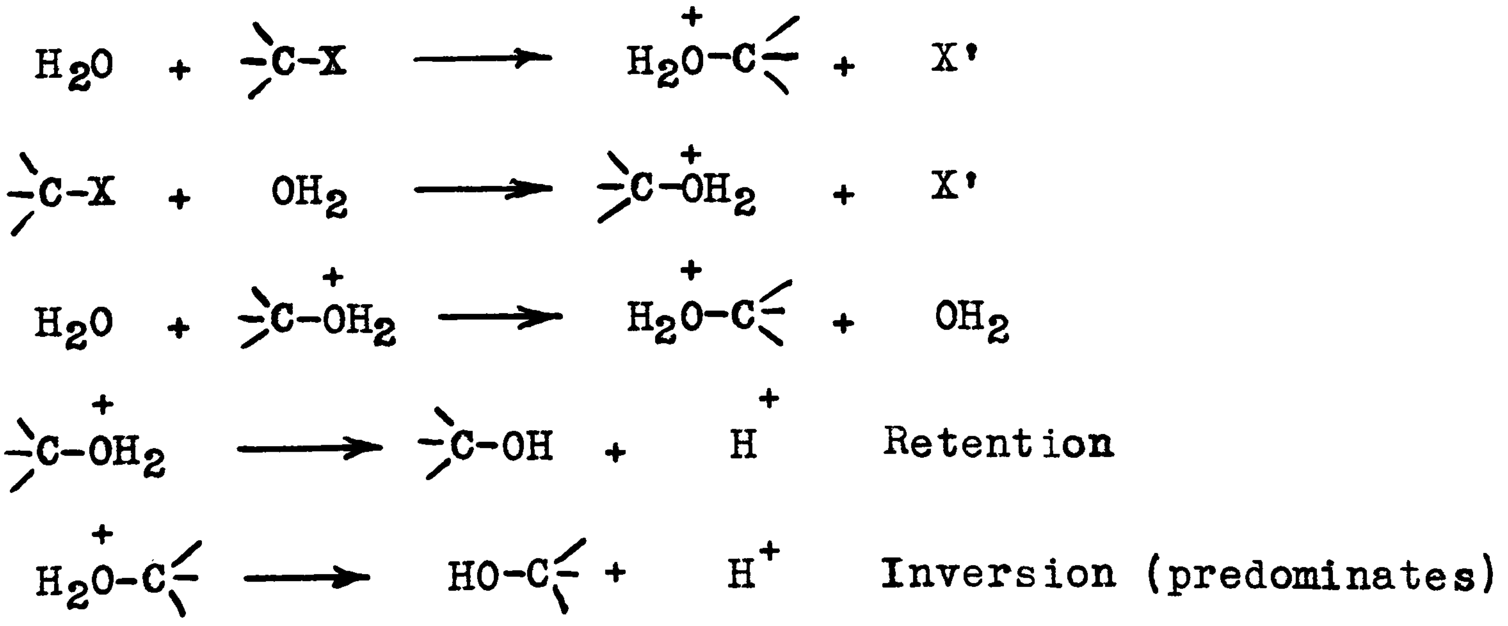
These investigators concluded from these results that only under special conditions such as temperature and solvent could triaryl substituted groups of the above type maintain even momentarily an asymmetric configuration. If a replacement occurred in such a manner as to involve the intermediate formation of an ion of the type  $\left[R_2{:}\overset{R_1}{\underset{R_3}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}}\right]^+$ racemized products would always result.

It must also be noted that the formation of a free radical of the type  $R_1{:}\overset{R_2}{\underset{R_3}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}}\cdot$ which is common in compounds such as the triaryl carbinols would probably also lead to racemization due to the formation of an intermediate planar configuration.

Now tertiary carbinols differ enormously from secondary carbinols in their greater reactivity with hydrogen halides. This suggests that the reaction goes by an entirely different mechanism. If the ion $R_3C^+$ were the intermediate for all tertiary carbinols as postulated by Wallis and Adams for triaryl carbinols, optically active tertiary halides would probably never be formed because of complete racemization of the positive ion.

The formation of the intermediate $R_3C^+$ might be expected in the case of tertiary alcohols since they act more like true bases with hydrogen halide than like secondary alcohols. Recent work by Bartlett (12) on the solvolysis of tertiary butyl chloride indicated that ionization was the rate determining step of the reaction. This would indicate that the hydrolysis of tertiary halides would result in a completely racemized alcohol due to the intermediate formation of the ion $R_3C^+$.

Based on a study of the hydrolytic reactions of tertiary butyl chloride Winstein (13) takes exception to the simple ionic mechanism of Ingold _et al_ (7) and proposes a mechanism in which the ions are hydrated as follows:-



References: (12) Bartlett, P.D. J. Am. Chem. Soc. 61 1630 (1939)

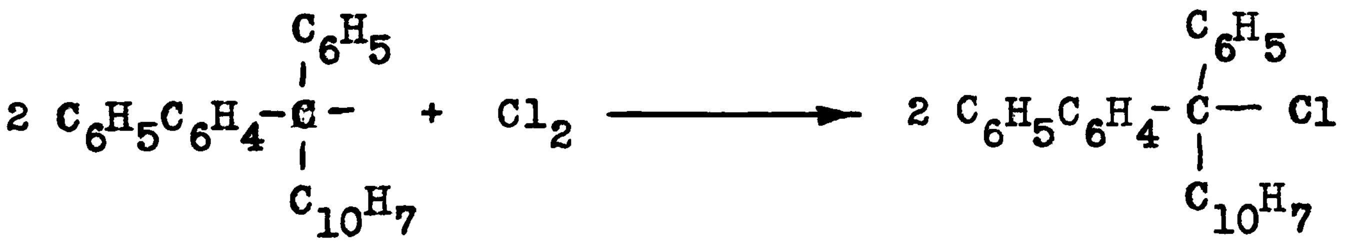
(13) Winstein, S. J.Am. Chem. Soc. 61 1635 (1939)

In this mechanism the solvent is considered as a reactant and the reaction is not monomolecular but multimolecular. This mechanism avoids the assumption of a true $-\overset{\diagdown}{\underset{\diagup}{C}}{}^{+}$ ion, and so racemization in the true sense does not necessarily take place.

As none of the above mechanisms permit any predictions to be made, it was necessary to study experimentally an optically active tertiary carbinol.

The work of Wallis and Adams (11) has been mentioned but the preparation of halides from the triaryl carbinols may involve the formation of free radicals and hence is not a good example.

Karagunis and Drikos (13 a) obtained tertiary halides which were feebly optically active by treating triaryl methyl radicals with chlorine under the action of circularly polarized light. For example the following reaction was carried out under the influence of both d- and l- circularly polarized light:



$$2\ C_6H_5C_6H_4-\overset{C_6H_5}{\underset{C_{10}H_7}{C}}- \ + \ Cl_2 \longrightarrow 2\ C_6H_5C_6H_4-\overset{C_6H_5}{\underset{C_{10}H_7}{C}}-Cl$$

At the end of about one hour, a maximum rotation of $\pm\ 0.08^{\circ}$ was obtained. However, after the reaction had gone to completion the product was inactive.

Reference: (13a) Karagunis and Drikos, Z. Physik. Chem. 26B, 428 (1934)

Simple aliphatic tertiary alcohols have never been resolved, so natural products had to be resorted to. A study of optically active tertiary alcohols from nature such as linalool indicated that optically active halides could be formed and that complete racemization did not apparently occur.

Vanin and Chernoyarova (14) reported the preparation of linalyl chloride using phosphorus trichloride and obtained what they considered to be linalyl chloride and of the opposite sign of rotation. They did not use pyridine in the reaction mixture.

$$\text{d-linalool} \xrightarrow[\text{smoothly}]{PCl_3} \text{l-linalyl chloride}$$

$$[\alpha]^{20}_{D} \ +10.12^{\circ} \qquad\qquad [\alpha]^{20}_{D} \ -1.74^{\circ}$$

They hydrolyzed the chloride to linalool as follows:-

$$\text{l-linalyl chloride} \xrightarrow[\text{KOH}]{\text{Alcoholic}} \text{l-linalool}$$

$$[\alpha]^{20}_{D} \ -2.62^{\circ} \qquad\qquad [\alpha]^{20}_{D} \ -1.58^{\circ}$$

No change in the sign of rotation was obtained on hydrolysis. The above transformations indicated that only one Walden inversion had apparently occurred and that considerable racemization had taken place in one or both of the reactions.

Reference: (14) Vanin I.I. and Charnoyarova A.A. J. Gen. Chem. U.S.S.R. 7, 885 (1937)

This case however was an unfortunate one because it is well established that linalool undergoes the typical allylic rearrangement to geraniol or its halide with acids. For example Dupont and Labaune (15) reported the formation of geranyl bromide from linalool and hydrogen bromide. This would destroy the asymmetry of the linalool since geraniol has no asymmetric carbon atom.

Furthermore Ikeda and Takeda (16) found that linalool on treatment with hydrogen chloride produced an optically active monocyclic terpene $\alpha_D = +21.32$ along with geraniol and other compounds.

There is also the possibility that that part of the linalool which did not rearrange might merely add one or two molecules of hydrogen chloride and thus yield halides which might be difficult to separate. This has been reported by Dupont and Labaune (17).

In any case no pure halide could be obtained and the results of Vanin and Chernoyarova are open to considerable doubt. This is especially true since they did not use pyridine in their reaction mixture and with phosphorus trichloride alone there is always some hydrogen chloride present and hence rearrangement products would be bound to appear. To avoid these uncertainties the use of completely hydrogenated linalool is much more preferable.

References: (15) Dupont, Labaune: Chem. Zentr II 734 (1910)

(16) Ikeda T., Takeda S., J.Chem.Soc. Japan 58, 80-7 (1937)

(17) Dupont, Labaune, Bericht von Roure-Bertrand Fils P. 21 Oct. (1909)

Tetrahydrolinalool was prepared by Enklaar (18) by hydrogenating linalool in the gaseous phase at 130-140°C over a nickel catalyst. Paal (19) and Barbier and Locquin (20) prepared it by hydrogenating linalool at room temperature using platinum black as the catalyst. These latter workers found the resulting tetrahydrolinalool to be laevorotatory. On the other hand Matuura (21) reports tetrahydrolinalool prepared by hydrogenation of laevorotatory linalool over nickel as being dextrorotatory. However the author states that this may be due to the presence of dextrorotatory camphor as an impurity.

Miss Gilbert (22) prepared tetrahydrolinalool one sample of which was laevo and another was dextrorotatory. This was probably due to the lack of proper equipment for fractionating the original linalool which may contain dextrorotatory camphor and other optically active impurities.

Miss Gilbert also found that her samples of tetrahydrolinalool whether laevo or dextro formed a chloride with fuming hydrochloric acid or with anhydrous hydrogen chloride, which when purified was slightly dextrorotatory. It is likely that these rotations are not significant because the original linalool used cannot be considered to be sufficiently pure.

This thesis deals with the preparation and reactions of tetrahydrolinalool and its chloride. Since the linalool used by Miss Gilbert could not have been pure, particular attention was paid to its purification in order that the rotations of the reduced linalool and its chloride would be significant.

References: (18) Enklaar, Rev. Trav. Chem. Pays Bas 27, 411 (1908)
(19) Paal C., Frdl. 13 627 (1923)
(20) Barbier, P. and Locquin R., Compt. Rendu. 158, 1554 (1914
(21) Matuura T., Jour. Sci. Hirosima Univ. Vol. 8 Mar.1938 No. 2
Gilbert, M.R. McGill Thesis, May (1938)

## (b) Outline of Problem

The linalool as received from Dr. Schuchardt and Co. was subjected to an intensive purification. This included a preliminary treatment with Tollens' reagent to remove aldehydes such as citronellal normally dextrorotatory ( $\alpha_D^{17.5} = +12.5$ ), followed by two fractional distillations using a column of thirteen theoretical plates. The residue from the first distillation was dextrorotatory and may be due to camphor ( $\alpha_D = +55.4$ ) or borneol ( $\alpha_D = +38.45$).

After two such distillations the physical properties of the various fractions were almost identical. The purified linalool now had the following properties:

$[\alpha]_D^{24}$ -18.19°; $d_4^{25}$ 0.8616; $N_D^{25}$ 1.4601;

M.R. found 49.01 Calc. 48.97.

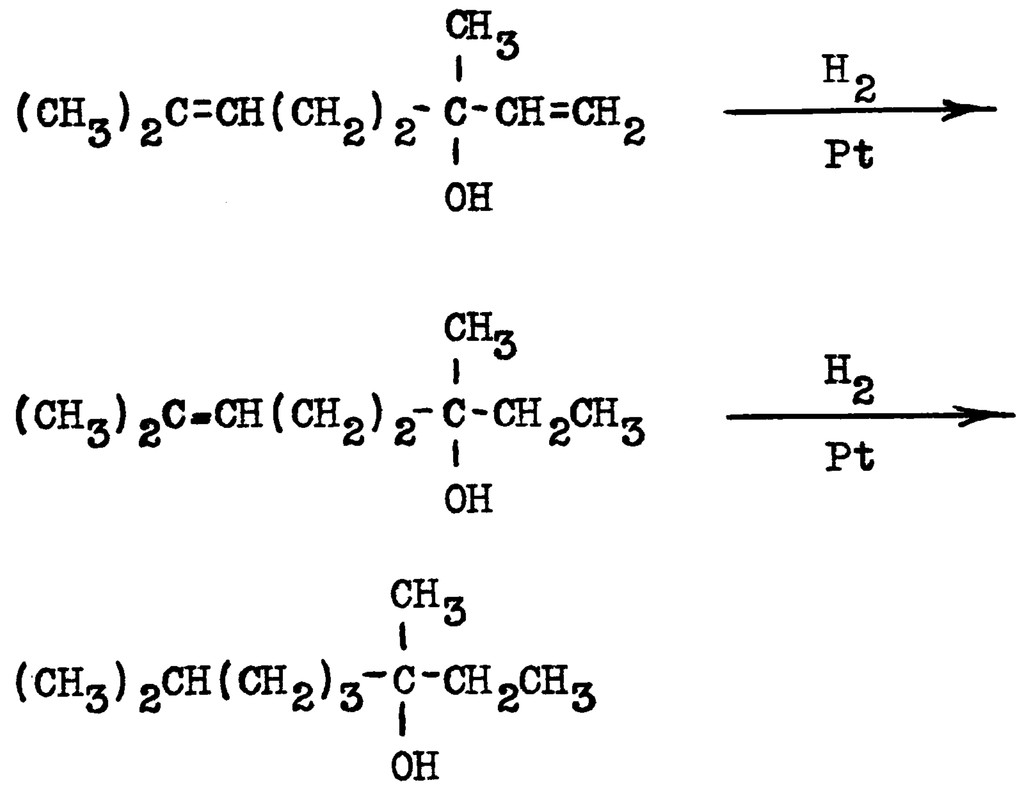
The maximum rotation for l-linalool reported in the literature is $[\alpha]_D^{20}$ -20.12° (22a). The value found above is very close to this figure, and this is probably close to the maximum rotation of linalool.

This linalool was hydrogenated directly at room temperature using Adams' platinum catalyst. The addition of hydrogen was stepwise, dihydrolinalool being formed first and on further hydrogenation tetrahydrolinalool was formed. When ethanol was used as a solvent the hydrogenation stopped with the formation of dihydrolinalool.

Reference: (22a) Tiemann: Ber. 31, 834 (1898)

Dupont et al (22b) reported this stepwise reduction using ethanol as the solvent and platinum as the catalyst. Miss Gilbert (22) however found abnormalities in this reduction as one of her samples was completely reduced in ethyl alcohol solution. This stepwise reduction shows the difference in activity of the double bonds.

To effect complete hydrogenation to tetrahydrolinalool Miss Gilbert used glacial acetic acid as the solvent. This may explain why some of her samples were dextrorotatory since it is possible that some rearrangement to optically active alpha terpineol may have occurred. To prevent this care was taken in this investigation not to use acidic media for the reduction. The following equations illustrate the hydrogenation reactions:-



Linalool $(CH_3)_2C=CH(CH_2)_2-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH=CH_2 \xrightarrow[Pt]{H_2}$

dihydrolinalool $(CH_3)_2C=CH(CH_2)_2-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_3 \xrightarrow[Pt]{H_2}$

tetrahydrolinalool $(CH_3)_2CH(CH_2)_3-\underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_3$

Reference: (22b) Dupont G., Desreux V., Dulou R., Bull. Soc. Chim. 4 2016 (1937)

The remaining unsaturated constituents which had a higher optical activity were removed by shaking with potassium permanganate solution followed by a treatment with dilute potassium carbonate solution to remove acids formed by the oxidation.

The tetrahydrolinalool was now purified by a fractional vacuum distillation in a modified Claisen flask followed by a vacuum fractionation through a column having 13 theoretical plates. The physical properties of the various fractions of the second distillation including the residue were all practically identical. Since the residue was laevorotatory and practically the same as the other fractions in value, there cannot be present any appreciable amounts of dextrorotatory impurities such as d-camphor.

This pure tetrahydrolinalool was laevorotatory with $[\alpha]^{23}_{D} = -0.55^{\circ}$; $d^{25}_{4} = 0.8250$; $N^{25}_{D} = 1.4320$.

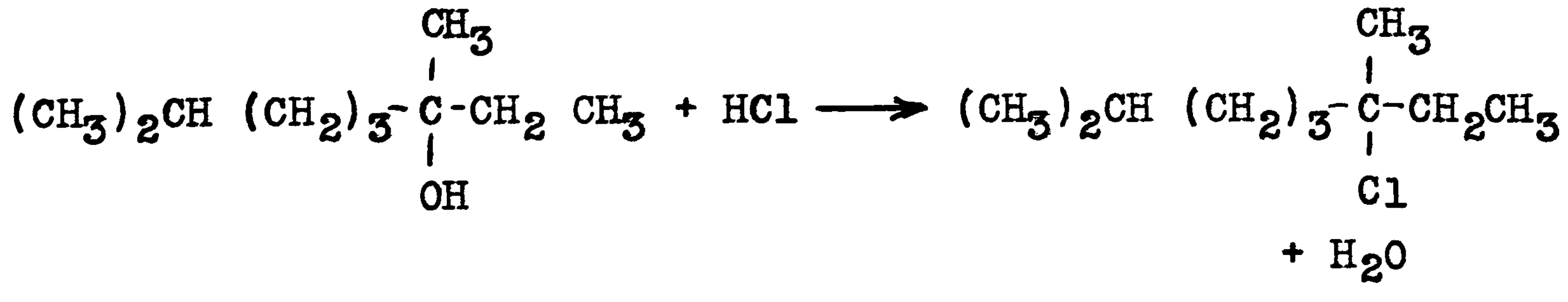
The following table shows a comparison of the physical constants obtained in this work with those obtained by other workers:

| Author | Reference | Temp. °C | $[\alpha]_D$ | Temp. °C | d | Tmp. °C | $N_d$ | B.P. °C | Press. mm. |
|---|---|---|---|---|---|---|---|---|---|
| Observed | This Thesis | 23 | -0.55 | 25/4 | 0.8250 | 25 | 1.4320 | 89.0 | 15 |
| Matuura | (19) | - | +0.65 | 25/4 | 0.8352 | 25 | 1.4369 | 87.5-88 | 13 |
| Barbier & Locquin | (18) | 17 | -0.47 | 0/4 | 0.851 | - | - | 86-88 | 10 |
| Paal | (21) | - | -0.78 | 16/4 | 0.8327 | - | - | 89 | 15 |
| Enklaar | (17) | - | - | 15/4 | 0.8360 | 15 | 1.4388 | 88-88.5 | 14 |
| Gilbert | (22) | 28 | ±0.11 | 20/4 | 0.8317 | 20 | 1.4374 | 78 | 8 |

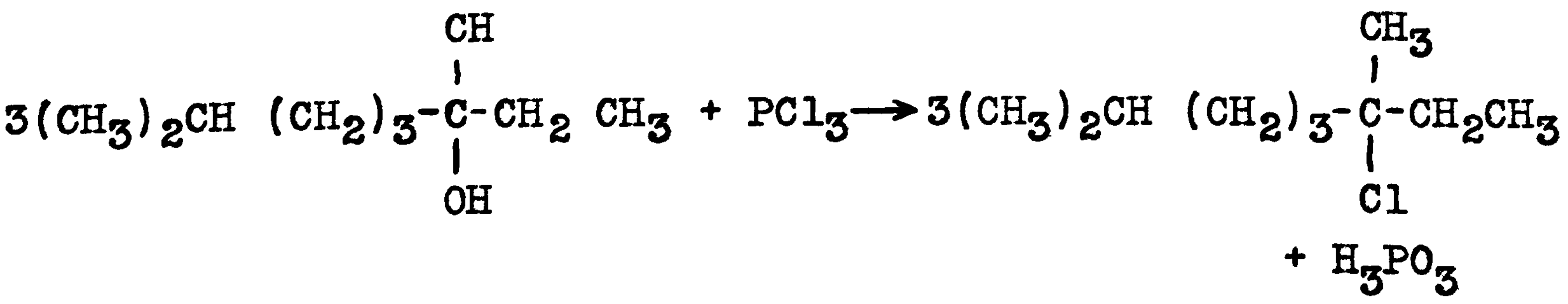
It is inconceivable that racemization or rearrangement could have occurred during the hydrogenation since no acid media was used and high temperatures were not employed. So the activity of the tetrahydrolinalool prepared as above must be close to the maximum if the maximum of the linalool has been found in nature.

The second molecule of hydrogen was hard to put in the linalool molecule and there was always left some unreacted dihydrolinalool. Great pains were taken to remove any residual dihydrolinalool and other unsaturated materials by the oxidation with potassium permanganate as mentioned before. This may explain why Paal (19) obtained a higher optical activity of tetrahydrolinalool than the value found in this investigation.

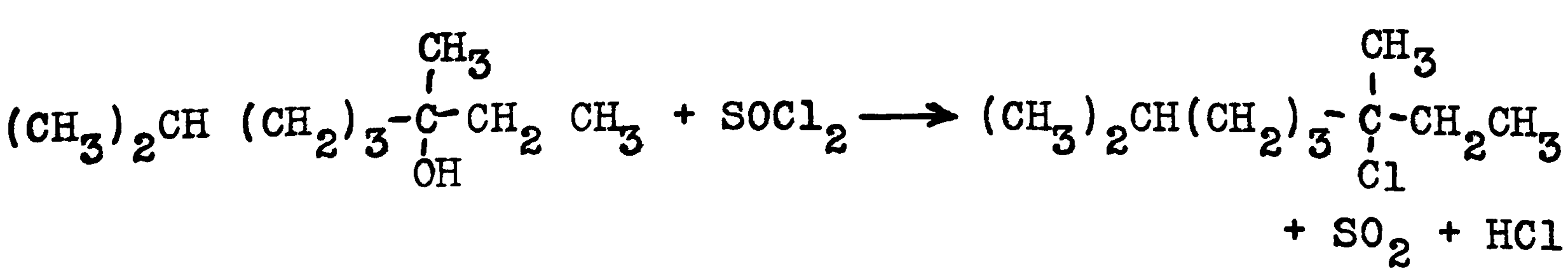
Tetrahydrolinalyl chloride was prepared from the purified tetrahydrolinalool using the reagents: HCl; $SOCl_2$; and $PCl_3$, under varying conditions. The following equations show the general reactions in each case:



$$\mathrm{(CH_3)_2CH\ (CH_2)_3-\overset{CH_3}{\underset{OH}{C}}-CH_2\ CH_3 + HCl \longrightarrow (CH_3)_2CH\ (CH_2)_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2CH_3 + H_2O}$$



$$\mathrm{3(CH_3)_2CH\ (CH_2)_3-\overset{CH}{\underset{OH}{C}}-CH_2\ CH_3 + PCl_3 \longrightarrow 3(CH_3)_2CH\ (CH_2)_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2CH_3 + H_3PO_3}$$



$$\mathrm{(CH_3)_2CH\ (CH_2)_3-\overset{CH_3}{\underset{OH}{C}}-CH_2\ CH_3 + SOCl_2 \longrightarrow (CH_3)_2CH(CH_2)_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2CH_3 + SO_2 + HCl}$$

The following table shows the results obtained with the above reagents under various conditions:-

| Reagent | Solvent | Temp °C | $\alpha_D$ | Temp. °C | Chlorine % Total | Chlorine % Tertiary | Unsaturation |
|---|---|---|---|---|---|---|---|
| Fuming HCl | None | 25 | -0.25 | 24 | 20.0 | 19.8 | Absent |
| $SOCl_2$ | None | -78 | 0.00 | 24 | 18.2 | - | Present |
| $SOCl_2$ | None | 25 | -0.02 | 24 | 18.8 | - | Present |
| $SOCl_2$ | 100 cc. $CCl_4$ | -15 | -0.13 | 24 | 17.6 | - | Present |
| $SOCl_2$ | 100 cc. $CCl_4$ | 25 | 0.00 | 24.5 | 18.6 | - | Present |
| $PCl_3$ | 100 cc. n-Pentane plus pyridine | -78 | -0.38 | 25 | 17.9 | - | Present |
| HCl gas | 100 cc. n-pentane | -78 | +0.26 | 25.5 | 14.7 | 14.5 | Absent |
| HCl gas | 100 cc. n-pentane | 25 | -0.28 | 23 | 19.8 | - | Absent |
| HCl gas | 100 cc. ether | -78 | -0.09 | 25 | 19.8 | - | Absent |

NOTE: The tetrahydrolinalool used in the above experiments had an $\alpha_D^{23} = -0.45^\circ$

$$[\alpha]_D^{23} = -0.55^\circ$$

: The theoretical percent chlorine in tetrahydrolinalyl chloride is 20.1%

Of the reagents used gaseous hydrogen chloride and fuming hydrochloric acid were the only ones which gave a pure chloride. The reagents phosphorus trichloride and thionyl chloride always gave a chloride contaminated with unsaturated compounds.

The chloride prepared from tetrahydrolinalool and fuming hydrochloric acid at room temperature was hydrolyzed by shaking with water at 25°C. A good deal of unsaturated products were formed. When these were removed with potassium permanganate the resulting tetrahydrolinalool had a rotation of $\alpha_D^{24}$ -0.12°. On distilling this alcohol more unsaturated compounds were formed.

In preparing the chloride using gaseous hydrogen chloride at -78°C in n-pentane solution a white crystalline precipitate was isolated. This was found to consist of a solid hydrate of hydrogen chloride. Its formation can be explained by the fact that water is formed in the reaction between hydrogen chloride and tetrahydrolinalool. This water reacts with hydrogen chloride and the resulting hydrate being insoluble in n-pentane crystallizes out. No crystals were formed when diethyl ether was used as a solvent at -78°C since the hydrate is soluble in ether and remains in solution. The approximate chlorine content of the crystals was determined and also the melting point. The following table shows a comparison between the chlorine content of the above crystals and of various hydrates of hydrogen chloride as reported by Rupert(22c) and also of the hypothetical addition compound of hydrogen chloride and tetrahydrolinalool postulated by Ingold _et al_ (7).

Reference: (22c) Rupert, J. Am. Chem. Soc. _31_ 851 (1909)

| Material | Chlorine % | Melting Point oC |
|---|---|---|
| White crystals | over 21.2 | -26 |
| $HCl \cdot H_2O$ | 65 | -15.35 |
| $HCl \cdot 2H_2O$ | 48.9 | -17.7 |
| $HCl \cdot 3H_2O$ | 39.2 | -24.4 |
| Tetrahydrolinalool HCl | 18.3 | ----- |

Due to difficulty in weighing the white solid without loss of hydrogen chloride the result for chlorine above must be too low. On warming to room temperature the crystals decomposed violently evolving hydrogen chloride gas. But decomposition yielded no organic substances but merely a water solution of hydrochloric acid, hence it must be concluded that the crystals consisted of some hydrate of hydrogen chloride and not a complex between tetrahydrolinalool and hydrogen chloride.

## (c) Discussion

By analogy with the work of Levene and Rothen (9) on the bromination of methyl, ethyl, and propyl, phenyl carbinols at -78°C where substitution was found to take place without a Walden's inversion it may be assumed that no inversion takes place when tetrahydrolinalool is changed to the corresponding chloride at -78°C using HCl gas as the chlorinating agent. The substitution was accompanied by a change in sign of rotation. This is unlike any aliphatic secondary alcohol so far reported.

When the substitution took place at 25°C no change in sign of rotation was obtained and inversion was the predominating reaction. This is similar to the results obtained from the bromination of the higher homologues of secondary phenyl carbinols reported by Levene and Mikeska (2) where no change in sign of rotation took place. However it was found that no inversion of configuration had occurred with these secondary carbinols.

When the laevorotatory chloride was hydrolyzed, a laevorotatory tetrahydrolinalool was formed. This indicated that a Walden's inversion had taken place. This agrees with the results obtained with secondary carbinols.

Phosphorus trichloride and tetrahydrolinalool produced mainly inversion in the formation of tetrahydrolinalyl chloride. Thionyl chloride produced both inversion and retention but slightly more inversion.

Reactions producing both inversion and retention no doubt always occur in negative substitution reactions of tertiary carbinols but one or the other usually predominates. There is probably only a very little racemization due to a common ion and likely there is only a little due to the formation of the unstable $R_3C^+$. If modern theories of substitution are correct the ion $R_3C^+$ probably never exists as such. Hydrogen chloride with B octanol gives some substitution of both types while phosphorus trichloride gives mainly inversion. In this respect tertiary alcohols resemble secondary carbinols. The great reactivity of tertiary alcohols over secondary alcohols must be due to the readiness with which the OH is removed, and not due to a different mechanism as might be predicted from the results of Conant, Kirner, and Hussey (23) who found that tertiary halides react slower with potassium iodide than most secondary halides.

The conclusion that tetrahydrolinalool showed no inversion of configuration in the reaction with hydrogen chloride when carried out in a solvent (n-pentane) at -78°C is not entirely in agreement with the findings of Levene and Rothen (8). They found that in the reaction of secondary carbinols with hydrogen bromide an inversion of configuration took place even at -78°C if the reaction was carried out in a solvent (such as aliphatic carbinols, diethyl ether and benzene). This may be due to the fact that they used an unsuitable solvent for when the experiment with tetrahydrolinalool was repeated using diethyl

Reference: (23) Conant, Kirner, Hussey J. Am. Chem. Soc. <u>47</u>, 476 (1925) ether as the solvent at -78°C an inversion of configuration was observed accompanied by considerable racemization.

The solvents that Levene and Rothen used all could form some complex with hydrogen halide.

The aliphatic carbinols and diethyl ether actually do form definite complexes (probably oxonium salts) with hydrogen halides; and benzene is known to form complexes with aluminium chloride at low temperatures and may do likewise with hydrogen halide. Hence these solvents would favour an ionic mechanism involving inversion, while pentane forming no complexes, and repressing ionization as much as possible, would favour retention.

Levene and Rothen report the formation of a white crystalline solid when secondary phenyl carbinols are made to react with hydrogen bromide at -78°C. They conclude that this is a solid addition compound probably of the structure of the intermediate postulated by Ingold (7). This conclusion has its only basis on the observation that at the melting point of the crystals (-20°C) water separates out.

A similar white solid was observed when tetrahydrolinalool was caused to react with hydrogen chloride at -78°C in n-pentane solution. On examination however it was found to consist of a hydrate of hydrogen chloride. It is possible that what Levene and Rothen observed was a solid hydrate of HBr since they report that it decomposes with violence on warming to room temperature. This must mean that a gas was given off, probably HBr since the mere decomposition into a liquid bromide and water would probably not have resulted in any visible reaction other than the change of state from liquid to solid.

Pickering (23a) reports solid hydrates of hydrogen bromide with the following melting points:-

$HBr \cdot 2H_2O$ -11.2°C; $HBr \cdot 3H_2O$ -48°C; $HBr \cdot 4H_2O$ -56°C

It is possible that some solid solution of HBr and $H_2O$ separated out in their experiments. This would account for their observation that over one mole of hydrogen bromide was absorbed by the carbinol. Their statement that water separated out when the crystals melted moreover cannot be correct since liquid water would not form at -20°C. The liquid which separated must have been a solution of hydrogen bromide in water.

Reference: (23a) Pickering, Phil. Mag. 36 111 (1893) V

## (d) Conclusion:

This work has now indicated that the replacement of OH by X in tertiary alcohols at 25°C. follows about the same course as that of secondary alcohols. For example this is illustrated by replacement accompanied by inversion predominating, particularly with phosphorus trichloride and pyridine and less so with thionyl chloride.

The fact that optically active tertiary halides are obtained shows that the idea of Winstein (13) and of Bartlett (12) is probably correct and that the ion $R_3C^+$ never actually exists at any time but it is solvated, thus protecting it from assuming a planar configuration, which would result in complete racemization.

We must assume then that tertiary alcohols and their halides undergo replacement reactions in the same way as secondary alcohols and that the great difference between the two classes is merely due to the difference in strength of the C-OH or C-X bond and not due to a different mechanism.

It then becomes difficult to understand the results of Conant, Kirner and Hussey (23) who reported that tertiary halides reacted slower than secondary halides with potassium iodide. We must assume that this reaction involves inversion, since it certainly does with secondary halides. If then inversion reactions appear hindered by shielding of the face centered bond by the three hydrocarbon residues we would then expect that the great speed of reaction of both halides and carbinols would be due to a replacement without inversion. However such, we have here shown, is not the case, for inversion, while not the only form of replacement, clearly predominates.

Possibly we must reinterpret Conant, Kirner and Hussey's results. They admit that the difference is not particularly great i.e. between secondary and tertiary halides, and this difference may not be nearly as significant as has been assumed by later workers. Furthermore these investigators used only one aliphatic tertiary halide and when we remember that isopropyl chloride reacted the slowest of all secondary halides, we may conclude that very likely the case of tertiary butyl chloride being the first member of the series is likewise anomolous. It would be of importance then to investigate higher tertiary halides and see if this difference in reactivity between secondary and tertiary halides was real or imaginary.

## (e) Summary

(1) A very pure form of tetrahydrolinalool was prepared by hydrogenating purified linalool at room temperature. The purified tetrahydrolinalool was found to be laevorotatory, in agreement with values reported by earlier investigators.

(2) Tetrahydrolinalyl chloride was prepared from this purified tetrahydrolinalool by the action of the reagents; hydrogen chloride (anhydrous and aqueous), thionyl chloride, and phosphorus trichloride. Hydrogen chloride was the only reagent which gave a pure chloride. The other reagents all produced tetrahydrolinalyl chloride contaminated with unsaturated compounds. Phosphorus trichloride produced mainly inversion of configuration while thionyl chloride was found to produce both inversion and retention with the inversion reaction slightly predominating.

Evidence was produced to show that at -78°C the preparation of tetrahydrolinalyl chloride using hydrogen chloride was associated with retention of configuration while the same experiment performed at room temperature resulted in an inversion of configuration.

(3) When the tetrahydrolinalyl chloride was hydrolyzed using water at 25°C the formation of the carbinol was accompanied by inversion of configuration along with racemization and olefin formation.

## Experimental

The linalool used in this investigation was obtained from Dr. Theodor Schuchardt Co. and had the following physical properties:-

| $d_4^{25}$ | $N_D^{25}$ | Mol.Ref. Calc. | Mol.Ref. Found | Tube Length dm. | [*] $\alpha_D^{26}$ | $[\alpha]_D^{26}$ | $(M)_D^{26}$ |
|---|---|---|---|---|---|---|---|
| 0.8627 | 1.4608 | 48.97 | 49.00 | 1 | -14.19° | -16.45° | -25.35° |

[*] Note: The $\alpha_D$ in every case in this thesis represents the rotation of one dm. even though sometimes measured in a two dm. tube.

### Preliminary Purification of Linalool:

This linalool was subjected to a preliminary purification by Tollens' reagent (24) to remove any aldehydes. The reagent was prepared as follows:-

To 20 grams silver nitrate in 100 cc. of water was added an equal volume of concentrated ammonium hydroxide. To this mixture was added an equal volume of 10% sodium hydroxide.

600 cc. of linalool were shaken with an equal volume of 1 : 1 Tollens' reagent in a 3 litre separatory funnel on a mechanical shaker for 3 hours. At the end of this period of time the lower aqueous layer was drawn off. This procedure was repeated three times using fresh portions of Tollens' reagent each time. The linalool layer was then filtered by suction to remove reduced silver. It was then shaken three times with dilute potassium carbonate solution to remove acids

Reference: (24) Norris J.F. "Experimental Organic Chemistry" 3rd Edn. (McGraw-Hill pub.) P.225

and three times with distilled water. Finally it was set aside over anhydrous potassium carbonate to remove any water.

A total of 1200 cc. of linalool was purified in this manner. The optical rotation measured in a 1 dm. tube was as follows:

$$\alpha^{26}_{D} = -14.26^{\circ}$$

First Distillation of Linalool:

1200 cc. of the dried linalool were vacuum distilled in an atmosphere of dry carbon dioxide through a fractionating column.

The column was packed with single turn glass helices and had an internal diameter of 0.75 ins. It was equipped with standard ground glass joints at the bottom to avoid all contamination. All rubber stoppers were boiled with 10% sodium hydroxide before use. The column head was of the total reflux variable take off type. The efficiency of the column as determined by the method given in Morton (25) using carbon tetrachloride and benzene was 13 theoretical plates. The column was surrounded by a heating jacket in series with a rheostat to control the temperature.

Reference: (25) Morton A.A. "Laboratory Technique in Organic Chemistry" 1st edn. (McGraw-Hill pub.) P.87

The following fractions were obtained:-

| Fraction | Pressure mm. | Temperature Oil Bath °C | Temperature Jacket °C | Temperature Head °C | Volume cc. |
|---|---|---|---|---|---|
| 1 | 15 | 110-115 | 88 | 88.5 | 40 |
| 2 | 15 | 110-115 | 88 | 89 | 13 |
| 3 | 15 | 110-115 | 88 | 90.0 | 1080 |
| Residue | - | - | - | - | 50 |

Physical properties of various fractions. Distillation 1.

| Frac. | Tube dm. | Temp. °C | $\alpha_D$ | $\alpha_D$ | $(M)_D$ | $d^{25}_4$ | $N^{25}_D$ | Mol.Ref. Calc. | Mol.Ref. Found | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 25 | -12.40 | -14.16 | -21.83 | 0.8756 | 1.4620 | 48.97 | 48.40 | Colourless |
| 2 | 1 | 25 | -15.05 | -17.31 | -26.68 | 0.8696 | 1.4602 | 48.97 | 48.56 | Colourless |
| 3 | 1 | 23.5 | -15.65 | -18.19 | -28.04 | 0.8604 | 1.4605 | 48.97 | 49.12 | Colourless |
| Residue (Redistilled) | 1 | 23.5 | + 6.67 | + 7.47 | +11.51 | 0.8934 | 1.4762 | 48.97 | 48.68 | Yellow, odour like that of geraniol |
| Residue of Residue | | - | - | - | - | - | 1.4918 | - | - | Very dark Brown. |

Second Distillation of Linalool:-

Fraction 3 (above) was redistilled in an atmosphere of dry carbon dioxide through the same column under the following conditions:-

| Fraction | Pressure mm. | Temperature Oil Bath °C | Temperature Jacket °C | Temperature Head °C | Volume cc. |
|---|---|---|---|---|---|
| 1 | 15 | 115-118 | 90 | 89.5 | 150 |
| 2 | 15 | 115-118 | 90 | 89.5 | 20 |
| 3 | 15 | 115-118 | 90 | 90 | 600 |
| 4 | 15 | 115-118 | 90 | 90 | 180 |
| | | - | - | - | 70 |

Physical properties of various fractions. Distillation 2.

| Frac. | Tube dm. | Temp. °C | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d_4^{25}$ | $N_D^{25}$ | Mol.Ref. Calc. | Mol.Ref. Found | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 25 | -15.16 | -17.62 | -27.16 | 0.8605 | 1.4601 | 48.97 | 49.07 | Colourless |
| 2 | - | - | - | - | - | 0.8620 | 1.4601 | 48.97 | 48.98 | Colourless |
| 3 | 1 | 24 | -15.67 | -18.19 | -28.03 | 0.8616 | 1.4601 | 48.97 | 49.01 | Colourless |
| 4 | 1 | 24 | -15.28 | -17.78 | -27.40 | 0.8595 | 1.4601 | 48.97 | 49.13 | Colourless |
| Residue | | 25 | -11.94 | -13.72 | -21.14 | 0.8706 | 1.4629 | 48.97 | 48.75 | Light yellow no geraniol odour. |

Fraction 3, Distillation 2 was used for the hydrogenation experiments.

Hydrogenation of Linalool

(a) In Ethyl Alcohol

The purified linalool (fraction 3, distillation 2) was hydrogenated using ethyl alcohol as the solvent and Adams' platinum oxide catalyst prepared according to Organic Synthesis.(26)

The hydrogenation apparatus consisted of a steel hydrogen reservoir tank equipped with a 50 pound pressure gauge. This tank was connected by heavy rubber tubing to a 500 cc. heavy wall glass pressure bottle. This bottle containing the liquid to be hydrogenated was mounted on a shaking device actuated by an electric motor. It was enclosed by a wire screen. All rubber connections were boiled with sodium hydroxide solution and swabbed inside with dry cotton.

Reference: (26) Adams, Coll. Vol. Org. Syn. (1932)
(John Wiley and Sons Pub.) P.452

The ethyl alcohol used as the solvent was purified as follows:-

750 cc. of 95% ethanol was refluxed with 75 grams sodium hydroxide and 7 grams of aluminum powder for one hour. The alcohol was then distilled over rejecting the first and last 100 cc. portions of the distillate.

The main fraction was then further purified by the method of Dunlap (27). One gram of silver nitrate was dissolved in the alcohol and 3 grams of potassium hydroxide in alcohol solution were added. The precipitated silver hydroxide was allowed to settle overnight. The alcohol was then decanted from the black residue and was distilled into a brown glass stoppered bottle.

This procedure was adopted to remove aldehydes which would poison the platinum catalyst.

For the hydrogenation, 75 cc. of purified linalool and 75 cc. of purified ethyl alcohol were placed in the bottle along with 0.2 grams Adams' platinum oxide catalyst. After the bottle had been evacuated and filled with hydrogen alternately three times to displace all the air, the hydrogenation was started. A curve (Fig. 1) was drawn to show the relation between pounds of hydrogen added and time of hydrogenation.

Using ethyl alcohol as the solvent, only one molecule of hydrogen (1 $H_2$) could be added to the linalool. The addition of more catalyst, shaking the mixture with air and the addition of more ethyl alcohol were all ineffective in producing a greater addition of hydrogen.

Reference: (27) Dunlap, J. Am. Chem. Soc. <u>28</u> 395 (1906)

The hydrogenated product, probably consisting of dihydrolinalool along with some tetrahydrolinalool and unchanged linalool in alcohol solution, was filtered from the platinum catalyst. It was shaken four times with large volumes of distilled water in a separatory funnel to remove the alcohol. This crude dihydrolinalool was set aside in a glass stoppered flask along with anhydrous potassium carbonate to remove any water. The optical rotation of the dried product measured in a 2 dm. tube was:-

$$\alpha_{D}^{23^{\circ}} = -1.74^{\circ}$$

(b) <u>Hydrogenation Using no Solvent</u>

75 cc. purified linalool were hydrogenated without any solvent using 0.3 grams Adams' platinum oxide catalyst. A typical hydrogenation curve is shown in Fig. 2. When the hydrogenation stopped before two equivalents of hydrogen had been absorbed, it was found that shaking the mixture with air was effective in reactivating the catalyst. If this failed, the addition of fresh catalyst would help the hydrogenation to go to completion. The time for complete hydrogenation varied from 5 to 20 hours for different batches. The purified linalool was hydrogenated in batches of 100 cc. using this method. The catalyst was removed by filtration. Several batches were combined to make 195 cc. of crude tetrahydrolinalool, probably containing dihydrolinalool and having the following physical properties:

| Tube dm. | Temp. °C | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d^{25}_4$ | $N^{25}_D$ | Mol.Ref. Calc. | Mol.Ref. Found | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 24 | -0.48 | -0.58 | -0.92 | 0.8274 | 1.4330 | 49.91 | 49.68 | Colourless |

Preliminary Purification of Tetrahydrolinalool

The unsaturated constituents were removed by shaking in a large separatory funnel with successive portions of 1% aqueous potassium permanganate. Fresh portions of permanganate were used until a pink colour persisted in the aqueous layer. About 7 grams of potassium permanganate were required to remove the unsaturation from 195 cc. of crude tetrahydrolinalool.

The oil was shaken with 2 one litre portions of water to remove the excess permanganate, and was then shaken with one litre of one percent aqueous potassium carbonate to remove any acids. The aqueous extract remained alkaline.

The tetrahydrolinalool was now washed with two one litre portions of distilled water, separated from the water layer, and filtered to remove any manganese dioxide. It was placed in a glass stoppered Erlenmeyer flask with 25 grams of anhydrous potassium carbonate and was allowed to stand overnight. The tetrahydrolinalool now showed the following physical properties:-

| Tube dm. | Temp. °C. | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d^{25}_4$ | $N^{25}_D$ | Mol.Ref. Calc. | Mol.Ref. Found | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 22 | -0.45 | -0.55 | -0.86 | 0.8254 | 1.4321 | 49.91 | 49.71 | Colourless |

## First Distillation of Tetrahydrolinalool

188 cc. of this purified tetrahydrolinalool were placed in a modified Claisen flask and vacuum distilled in an atmosphere of dry carbon dioxide under the following conditions:

| | | Temperature | | |
|---|---|---|---|---|
| Fraction | Pressure mm. | Bath °C. | Head °C. | Volume cc. |
| 1 | 4 | 88-90 | 68 | 10 |
| 2 | 4 | 88-90 | 68 | 150 |
| 3 | 4 | 88-90 | 68 | 15 |
| Residue | - | - | - | 10 |

Physical Properties of Various Fractions. Distillation 1.

| Frac. | Tube dm. | Temp. °C | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d_4^{25}$ | $N_D^{25}$ | Mol.Ref. Calc. | Mol.Ref. Found | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 23 | -0.38 | -0.46 | -0.73 | 0.8249 | 1.4322 | 49.91 | 49.75 | Colourless |
| 2 | 2 | 23 | -0.46 | -0.56 | -0.89 | 0.8250 | 1.4325 | 49.91 | 49.78 | Colourless |
| 3 | 2 | 23 | -0.47 | -0.57 | -0.90 | 0.8254 | 1.4322 | 49.91 | 49.72 | Colourless |
| Residue | 2 | 23 | -0.54 | -0.65 | -1.03 | 0.8282 | 1.4333 | 49.91 | 49.67 | Colourless |

## Second distillation of Tetrahydrolinalool

Fraction 2 above (150 cc.) was put through the long column under the following conditions:-

| Fraction | Pressure mm. | Temperature<br>Bath °C | <br>Head °C | <br>Jacket °C | Volume cc. |
|---|---|---|---|---|---|
| 1 | 15 | 123-125 | 88.8 | 92 | 10 |
| 2 | 15 | 123-125 | 89.0 | 92 | 120 |
| 3 | 15 | 123-125 | 89.0 | 92 | 12 |
| Residue | - | - | - | - | 5 |

An atmosphere of dry carbon dioxide was used as before.

Physical Properties of Fractions. Distillation 2.

| Frac. | Tube dm. | Temp. °C. | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d^{25}_{4}$ | $N^{25}_{D}$ | Mol.Ref. Calc. | Mol.Ref. Found | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 23 | -0.41 | -0.50 | -0.79 | 0.8251 | 1.4326 | 49.91 | 49.78 | Colourless |
| 2 | 2 | 23 | -0.45 | -0.55 | -0.87 | 0.8250 | 1.4320 | 49.91 | 49.75 | Colourless |
| 3 | 2 | 23 | -0.41 | -0.50 | -0.79 | 0.8255 | 1.4325 | 49.91 | 49.75 | Colourless |
| Residue | 2 | 23 | -0.42 | -0.51 | -0.81 | 0.8244 | 1.4328 | 49.91 | 49.84 | Colourless |

Fraction 2 of this distillation was used for the preparation of the chloride by different methods. This fraction did not show any unsaturation when tested with aqueous permanganate or bromine in acetic acid.

### Preparation of Tetrahydrolinalyl Chloride
### Using Aqueous Hydrochloric Acid at Room Temperature

100 cc. of concentrated hydrochloric acid were placed in a 200 cc. pyrex tube. This was immersed in a cooling bath

maintained at -20°C. Hydrogen chloride gas generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid was bubbled into the acid in the tube until it was saturated. 20 cc. of purified tetrahydrolinalool ( $\alpha_D^{23} = -0.45°$) were pipetted on top of the acid.

The tube was allowed to stand 2 hours at -20°C. when it was sealed off. It was placed in a water bath at 20°C. for 15 minutes and then placed in a shaking machine for three hours after wrapping in a cloth. It was allowed to stand overnight at room temperature. The tube and its contents were replaced in the cooling bath at -20°C. and after one hour it was opened. The tetrahydrolinalyl chloride layer was drawn off and washed in a separatory funnel successively with five 20 cc. portions of concentrated hydrochloric acid, ice water, and finally with ice cold sodium bicarbonate solution. The chloride was then separated and dried over anhydrous potassium carbonate. The latter was filtered off and the tetrahydrolinalyl chloride was vacuum distilled under the following conditions:-

| Bath Temp. °C. | Pressure mm. | Receiver Temp.°C. | Volume cc. |
|---|---|---|---|
| 30 | 0.04-0.07 | 0° | 13 |

No bubbler tube was used and the entire liquid came over without boiling. A small colourless residue of about

0.5 cc. was left in the flask. The distillate showed the following physical properties:-

| Tube dm. | Temp. °C. | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d_4^{25}$ | $N_D^{25}$ | Mol.Ref. Calc. | Mol.Ref. Found | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 23 | -0.24 | -0.28 | -0.49 | 0.8639 | 1.4343 | 53.25 | 53.28 | Colourless<br>No odour<br>of HCl |

The chloride was then fractionated in an atmosphere of dry carbon dioxide using a modified Claisen flask distillation assembly equipped with ground glass joints.

| Fraction | Pressure mm. | Oil Bath °C. | Head °C. | Volume cc. |
|---|---|---|---|---|
| 1 | 8 | 100-102 | 70 | 1 |
| 2 | 8 | 100-102 | 70.5 | 9 |
| Residue | - | - | - | 2 |

The various fractions showed the following properties:-

| Fraction | Tube dm. | Temp. °C. | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d_4^{25}$ | $N_D^{25}$ | Mol.Ref. Calc. | Mol.Ref. Found |
|---|---|---|---|---|---|---|---|---|---|
| 1 | - | - | - | - | - | - | 1.4342 | - | - |
| 2 | 2 | 24 | -0.25 | -0.28 | -0.51 | 0.8643 | 1.4341 | 53.25 | 53.23 |
| Residue | 1 | 22.5 | -0.25 | -0.29 | -0.51 | 0.8639 | 1.4342 | 53.25 | 53.27 |

Fraction 2 showed no unsaturation on testing with a solution of bromine in acetic acid.

Analysis of fraction 2, above, for chlorine:-

| Total Chlorine | | | Tertiary Chlorine | | | |
|---|---|---|---|---|---|---|
| Sample Weight gms. | AgCl Weight gms. | Chlorine % | Sample Weight gms. | Volume $\frac{N}{10}$ NaOH ml. | Chlorine % | Theoretical Chlorine % |
| 1.1578 | 0.9342 | 20.0 | 0.4405 | 24.49 | 19.8 | 20.1 |

The <u>total chlorine</u> was determined by weighing out about one gram of the chloride to 0.1 milligram into a 400 cc. beaker containing 200 cc. of ethyl alcohol purified by distillation from silver nitrate. About 100 cc. of a one per cent filtered alcoholic silver nitrate solution were slowly run into the beaker with constant stirring. The precipitated silver chloride was allowed to settle overnight in the dark. It was then filtered off and weighed in a Gooch crucible and the percentage chlorine in the sample was calculated in the usual manner.

The <u>tertiary chlorine</u> was determined according to the method of Michael and Leopold (28). About 0.5 gram of the tetrahydrolinalyl chloride was weighed to 0.1 milligram into a 3 litre separatory funnel containing one litre of distilled water made neutral to methyl red indicator. The funnel was stoppered and placed on a shaking machine for five hours.

Reference: (28) Michael and Leopold: Ann. der Chemie
<u>379</u>, 287 (1911)

At the end of this period the solution was titrated in the funnel with standardized tenth normal sodium hydroxide solution using methyl red as the indicator. Further shaking did not produce any acidity so the hydrolysis was considered to be complete. From the amount of standard sodium hydroxide used the amount of hydrochloric acid produced was determined. From this the chlorine hydrolyzable under the above conditions (the tertiary chlorine) was calculated.

### Hydrolysis of Tetrahydrolinalyl Chloride

4.450 grams of the chloride were weighed to the nearest milligram into a five litre separatory funnel containing four litres of distilled water. This was shaken on a shaking machine for 18 hours. At the end of this time a 200 ml. aliquot part of the aqueous layer was titrated with tenth normal sodium hydroxide. A titration of 12.41 ml. was obtained. This corresponded to 19.8% Cl so the hydrolysis was considered to be complete.

The mixture was extracted twice with purified ether. The ether extract was shaken with a one percent potassium permanganate solution until a pink colour persisted in the aqueous layer. Considerable unsaturation was indicated. It was then shaken with potassium carbonate solution and finally with distilled water. Manganese dioxide was filtered off and the ether was pumped off in vacuo at room temperature. The slightly yellow residue was dried over anhydrous potassium carbonate.

The optical rotation (1 dm. tube) was

$$\alpha_D^{24} = -0.12^\circ$$

No test for chlorides was obtained with alcoholic silver nitrate solution.

1 cc. of the hydrolyzed alcohol was distilled under the following conditions in an atmosphere of dry carbon dioxide.

| Fraction | Temperature Bath °C | Temperature Head °C | Pressure mm. | $N_D^{25}$ | Volume cc. | Remarks |
|---|---|---|---|---|---|---|
| 1 | 100 | 71 | 8 | 1.4314 | 0.5 | Colourless |
| Residue | - | - | - | - | 0.3 | Dark Yellow |

The distillate had developed unsaturation as shown by testing with a solution of bromine in glacial acetic acid.

## Preparation of Tetrahydrolinalyl Chloride Using Thionyl Chloride.

### (a) At -78°C. Using no Solvent.

Three grams of purified tetrahydrolinalool ( $\alpha_D^{23} = -0.45^\circ$) were mixed in a test tube at -78°C. with 3.6 cc. of thionyl chloride which had been purified by distillation.

This represented a ratio of 2.5 moles of thionyl chloride to 1 mole of tetrahydrolinalool. On adding the thionyl chloride the solution became deep pink in colour. After remaining in a dry ice bath at -78°C. for 16 hours the contents of the tube were poured into 10 cc. of ice water. A colourless oil floated to the top. This was extracted in a separatory funnel with carbon tetrachloride purified according to the method of Fieser (29). The extract was shaken successively with three 25 cc. portions of concentrated hydrochloric acid, once with water and once with saturated sodium bicarbonate. Most of the water layer was separated and the carbon tetrachloride extract was dried with anhydrous potassium carbonate in a glass stoppered flask.

The carbon tetrachloride was removed by evaporation *in vacuo* in a distilling flask at room temperature. The tetrahydrolinalyl chloride was then distilled in an atmosphere of dry carbon dioxide under the following conditions:

| | | Temperature | | | |
|---|---|---|---|---|---|
| Fraction | Pressure mm. | Bath °C. | Head °C. | Volume cc. | Remarks |
| 1 | 8 | 100 | 70 | 2 | Colourless |
| Residue | - | - | - | 0.5 | Dark Yellow |

The above fraction had the following properties:

| Fraction | Tube Length dms. | Temp. °C. | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d_4^{25}$ | $N_D^{25}$ | Mol.Ref. Calc. | Mol.Ref. Found |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 24 | 0.00 | 0.00 | 0.00 | 0.8551 | 1.4336 | 53.25 | 53.75 |
| Residue | - | - | - | - | - | - | 1.4390 | - | - |

Both the distillate and the residue showed unsaturation on testing with a solution of bromine in acetic acid.

Reference: (29) Fieser L. "Experiments in Organic Chemistry" 1935
(D.C. Heath & Co. Pub.) P.308

Analysis of Distillate (above) for Chlorine.

| Total Chlorine |  |  |  |
|---|---|---|---|
| Sample Weight gms. | AgCl Weight gms. | Chlorine % | Theoretical Chlorine % |
| 0.6112 | 0.4493 | 18.2 | 20.1 |

(b) <u>At 25°C. Using no Solvent</u>

The above experiment was repeated at room temperature. After removing the carbon tetrachloride by evacuation at 25°C. the chloride was distilled in an atmosphere of dry carbon dioxide with results as follows:-

| Fraction | Pressure mm. | Bath Temp. °C | Head Temp. °C | Volume cc. | Remarks |
|---|---|---|---|---|---|
| 1 | 6.5 | 115 | 66 | 2 | Colourless |
| Residue | - | - | - | 0.5 | Dark Yellow |

The above fractions had the following properties:-

|  |  |  |  |  | Total Chlorine |  |  |  |
|---|---|---|---|---|---|---|---|---|
| Fraction | Tube Length dms. | Temp. °C. | $\alpha_D$ | $N_D^{25}$ | Sample Weight gms. | AgCl Weight gms. | Chlorine % | Theoretical Chlorine % |
| 1 | 1 | 24 | -0.02 | 1.4348 | 0.2483 | 0.1886 | 18.8 | 20.1 |
| Residue | - | - | - | 1.4360 | - | - | - | - |

Both the distillate and residue showed unsaturation on testing with a solution of bromine in acetic acid.

### (c) In Carbon Tetrachloride at -15°C.

The above experiment was repeated using the same amounts of thionyl chloride and tetrahydrolinalool ($\alpha_D^{23} = 0.45^\circ$) in 100 cc. of purified carbon tetrachloride at -15°C. After standing at this temperature for 16 hours the solution was worked up as before. After removing the carbon tetrachloride from the solution the chloride was distilled in an atmosphere of dry carbon dioxide with results as follows:-

| Fraction | Pressure mm. | Temperature Bath °C | Temperature Head °C | Volume cc. | Remarks |
|---|---|---|---|---|---|
| 1 | 8 | 115 | 68 | 0.25 | Colourless |
| 2 | 8 | 115 | 68 | 2.0 | Colourless |
| Residue | - | - | - | 0.5 | Yellow |

The above fractions had the following properties:-

| Fraction | Tube Length dms. | Temp. °C. | $\alpha_D$ | $N_D^{25}$ | Total Chlorine Sample Weight gms. | Total Chlorine AgCl Weight gms. | Total Chlorine Chlorine % | Theoretical Chlorine % |
|---|---|---|---|---|---|---|---|---|
| 1 | - | - | - | 1.4270 | - | - | - | - |
| 2 | 1 | 24 | -0.13 | 1.4340 | 0.5104 | 0.3626 | 17.6 | 20.1 |
| Residue | - | - | - | 1.4360 | - | - | - | - |

All the above fractions showed unsaturation when tested with a solution of bromine in acetic acid.

(d) In Carbon Tetrachloride at 25°C.

The tetrahydrolinalyl chloride, prepared as in experiment (c) above, was distilled under the following conditions:

| Fraction | Pressure mm. | Temperature Bath °C. | Temperature Head °C. | Volume cc. | Remarks |
|---|---|---|---|---|---|
| 1 | 9 | 115 | 69 | 0.5 | Colourless |
| 2 | 9 | 115 | 69 | 2.0 | Colourless |
| Residue | - | - | - | 0.25 | Dark Yellow |

The fractions had the following properties:-

| Fraction | Tube Length dms. | Temp. °C. | $\alpha_D$ | $N_D^{25}$ | Total Chlorine Sample Weight gms. | Total Chlorine AgCl Weight gms. | Total Chlorine Chlorine % | Theoretical Chlorine % |
|---|---|---|---|---|---|---|---|---|
| 1 | - | - | - | 1.4305 | - | - | - | - |
| 2 | 1 | 24.5 | 0.00 | 1.4343 | 0.4397 | 0.3298 | 18.6 | 20.1 |
| Residue | - | - | - | 1.4378 | - | - | - | - |

All the above fractions showed unsaturation when tested with a solution of bromine in acetic acid.

## Preparation of Tetrahydrolinalyl Chloride Using Phosphorus Trichloride and Pyridine in n-pentane Solution at -78°C.

Five cc. of tetrahydrolinalool ( $\alpha_D^{23}$ = -0.45°), one cc. of dry pyridine and 6 cc. n-pentane distilled from phosphorous pentoxide were cooled in a tube to -78°C. in a dry ice bath for one hour. 2.2 cc. of phosphorous trichloride purified by distillation were added dropwise. A white precipitate formed immediately. After remaining 16 hours at -78°C. the mixture was poured into ice water and the tetrahydrolinalyl chloride was extracted with n-pentane. The extract was dried with anhydrous potassium carbonate and the n-pentane was removed in vacuo at room temperature. The chloride was then distilled in an atmosphere of dry carbon dioxide with the following results:-

| Fraction | Pressure mm. | Temperature Bath °C. | Temperature Head °C. | Volume cc. | Remarks |
|---|---|---|---|---|---|
| 1 | 7.5 | 120 | 50-68 | 0.5 | Colourless |
| 2 | 8 | 120 | 68 | 2.5 | Colourless |
| Residue | - | - | - | 0.2 | Yellow |

The above fractions had the following properties:-

| Fraction | Tube Length dms. | Temp. °C. | $\alpha_D$ | $N_D^{25}$ | Total Chlorine Sample Weight gms. | Total Chlorine AgCl Weight gms. | Total Chlorine Chlorine % | Theoretical Chlorine % |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 25 | -0.28 | 1.4270 | 0.3554 | 0.0544 | 3.8 | 20.1 |
| 2 | 1 | 25 | -0.38 | 1.4331 | 0.3214 | 0.2321 | 17.9 | 20.1 |
| Residue | - | - | - | 1.4391 | - | - | - | - |

All the above fractions showed unsaturation on testing with a solution of bromine in acetic acid.

## Preparation of Tetrahydrolinalyl Chloride Using Gaseous Hydrogen Chloride.

### (a) In N-pentane at -78°C.

Hydrogen chloride gas, dried by passing through concentrated sulphuric acid and a dry ice trap, was passed into a solution of purified tetrahydrolinalool ( $\alpha_D^{23} = -0.45^\circ$) in n-pentane for various periods of time. The n-pentane solution was contained in a 50 cc. distilling flask protected at the exit end with a calcium chloride drying tube. The flask was immersed in a carbon dioxide acetone cooling bath at -78°C.

The following table shows the conditions under which the chloride was prepared:-

| Experiment | Tetrahydrolinalool Used cc. | n-Pentane Used cc. | Time of Passing HCl Hours | Remarks |
|---|---|---|---|---|
| 1 | 5 | 10 | 1 | - |
| 2 | 4.5 | 10 | 9 | White crystals on bottom of flask |
| 3 | 6 | 95 | 27 | White crystals on bottom of flask. |

After the hydrogen chloride had been passed in for the specified time, the pentane solution was poured into 10 cc.

of ice water. The solution was washed as before with concentrated hydrochloric acid, water and sodium bicarbonate solution. It was dried over anhydrous potassium carbonate. In the case of experiment 3 (above) the solution was filtered from the white crystals before working up.

After removing the n-pentane in vacuo at room temperature in a distilling flask, the tetrahydrolinalyl chloride was distilled as follows:-

| Experiment | Fraction No. | Pressure mm. | Bath °C | Head °C | Volume cc. | Remarks |
|---|---|---|---|---|---|---|
| 1 | 1 | 7 | 118 | 67 | 0.25 | Colourless |
| | 2 | 7 | 118 | 67-68 | 2.5 | Colourless |
| | Residue | - | - | - | 2 | Colourless |
| 2 | 1 | 8 | 108 | 68.5-69 | 0.5 | colourless |
| | 2 | 8 | 108 | 69-70 | 3.5 | Colourless |
| | Residue | - | - | - | 0.3 | Colourless |
| 3 | 1 | 8 | 100 | 70 | 0.5 | Colourless |
| | 2 | 8 | 100-105 | 70 | 3.5 | Colourless |
| | Residue | - | - | - | 1 | Colourless |

The various fractions had the following properties:

| Experiment | Fraction | Tube Length dm. | Temp. °C. | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d^{25}_{4}$ | $N^{25}_{D}$ | Mol.Ref. Found | Mol.Ref. Calc. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | - | - | - | - | - | - | 1.4330 | - | - |
| | 2 | 1 | 22 | +0.06 | - | - | - | 1.4329 | - | - |
| | Residue | - | - | - | - | - | - | 1.4323 | - | - |
| 2 | 1 | - | - | - | - | - | - | 1.4340 | - | - |
| | 2 | 1 | 24 | +0.17 | +0.20 | +0.35 | 0.8516 | 1.4340 | 54.02 | 53.25 |
| | Residue | - | - | - | - | - | - | 1.4334 | - | - |
| 3 | 1 | - | - | - | - | - | - | 1.4330 | - | - |
| | 2 | 1 | 25.5 | +0.26 | +0.31 | +0.54 | 0.8521 | 1.4330 | 53.88 | 53.25 |
| | Residue | - | - | - | - | - | - | 1.4326 | - | - |

None of the above fractions showed unsaturation when tested with a solution of bromine in acetic acid.

The following table shows the percentage of chlorine in the various fractions tested:

| | | Total Chlorine | | | Tertiary Chlorine | | | |
|---|---|---|---|---|---|---|---|---|
| Exp. | Frac. | Sample Weight gms. | AgCl Weight gms. | Chlorine % | Sample Weight gms. | Volume N/10NaOH ml. | Chlorine % | Theoretical Chlorine % |
| 1 | 2 | 0.4611 | 0.2626 | 14.1 | - | - | - | 20.1 |
| 2 | 2 | 0.5339 | 0.3237 | 15.0 | - | - | - | 20.1 |
| 3 | 2 | 0.3040 | 0.1801 | 14.7 | 0.6097 | 24.94 | 14.5 | 20.1 |

**Examination of White Crystals:**

The white crystals which were filtered from the n-pentane solution in experiment (3) above were washed three times with n-pentane at -78°C. and as much as possible of the n-pentane was removed *in vacuo* at -78°C. The crystals were analyzed for chlorine by the following procedure:

About 0.1 grams of the dried crystals were weighed out as rapidly as possible into a beaker containing ethyl alcohol. The chlorides were precipitated with silver nitrate and the silver chloride was weighed in the usual manner after settling overnight in the dark.

Difficulty was encountered in weighing out the crystals as considerable hydrogen chloride gas was liberated so the result for chlorine must be low.

Melting Point: A portion of the crystals covered with n-pentane was allowed to warm up from -78°C. They were found to melt sharply with an evolution of hydrogen chloride gas.

The following table shows details of the analysis, the melting point and a comparison with other possible solids:

| Total Chlorine | | | |
|---|---|---|---|
| Sample Weight gms. | AgCl Weight gms. | Chlorine % | Melting Point °C |
| 0.0959 | 0.0823 | 21.2 | -26 |
| Calculated for: | | | |
| | $HCl \cdot H_2O$ | 65 | -15.35 |
| | $HCl \cdot 2\ H_2O$ | 48.9 | -17.7 |
| | $HCl \cdot 3H_2O$ | 39.2 | -24.4 |
| Tetrahydrolinalool·HCl | | 18.3 | - |

The liquid formed from the melted crystals was insoluble in n-pentane and remained as a separate layer on the bottom of the flask. On testing this lower layer with calcium carbide it was found to consist mainly of water. It was found moreover to be strongly acid and a test with silver nitrate solution indicated the presence of appreciable amounts of chlorides.

The supernatant n-pentane layer was evaporated at room temperature in vacuo in a tared flask. No residue was detected.

(b) In n-pentane at Room Temperature.

The chloride was prepared at room temperature using 5 cc. tetrahydrolinalool ( $\alpha_D^{23} = -0.45^\circ$) and 10 cc. n-pentane. No white crystals were formed. After passing in hydrogen chloride for five hours and allowing the solution to stand overnight it was worked up as before and the n-pentane was removed under vacuum. The resulting chloride was fractionated as follows:

| | | Temperature | | | |
|---|---|---|---|---|---|
| Fraction | Pressure mm. | Bath °C | Head °C | Volume cc. | Remarks |
| 1 | 9 | 100-105 | 70-71 | 0.5 | Colourless |
| 2 | 9 | 100-105 | 71 | 3.5 | Colourless |
| Residue | - | - | - | 0.3 | Colourless |

The various fractions had the following properties:

| Frac. | Tube Length dm. | Temp. °C. | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d_4^{25}$ | $N_D^{25}$ | M.R. Calc. | M.R. Found |
|---|---|---|---|---|---|---|---|---|---|
| 1 | - | - | - | - | - | - | 1.4343 | - | - |
| 2 | 1 | 23 | -0.28 | -0.32 | -0.57 | 0.8647 | 1.4346 | 53.25 | 53.26 |
| Residue | - | - | - | - | - | - | 1.4348 | - | - |

None of the above fractions showed unsaturation on testing with a solution of Bromine in acetic acid.

Fraction (2) was analyzed for total chlorine with results as follows:-

| Total Chlorine<br>Sample Weight gms. | Total Chlorine<br>AgCl Weight gms. | Total Chlorine<br>Chlorine % | Theoretical Chlorine % |
|---|---|---|---|
| 0.4606 | 0.3694 | 19.8 | 20.1 |

(c) <u>In Ether at -78°C.</u>

The chloride was prepared as before using 6 cc. tetrahydrolinalool ($\alpha_D^{23}$ = -0.45°) and 100 cc. diethyl ether distilled from sodium and phosphorus pentoxide. Dry hydrogen chloride was passed in for 14 hours at -78°C. No white crystals were formed. The solution was worked up in the usual manner and the ether was removed <u>in vacuo</u> at room temperature. The resulting chloride was distilled under the following conditions:-

| Fraction | Pressure mm. | Temperature | | Volume cc. | Remarks |
|---|---|---|---|---|---|
| | | Bath °C | Head °C | | |
| 1 | 9 | 100-105 | 70-71 | 1 | Colourless |
| 2 | 9 | 100-105 | 71 | 3.5 | Colourless |
| Residue | - | - | - | 1 | Colourless |

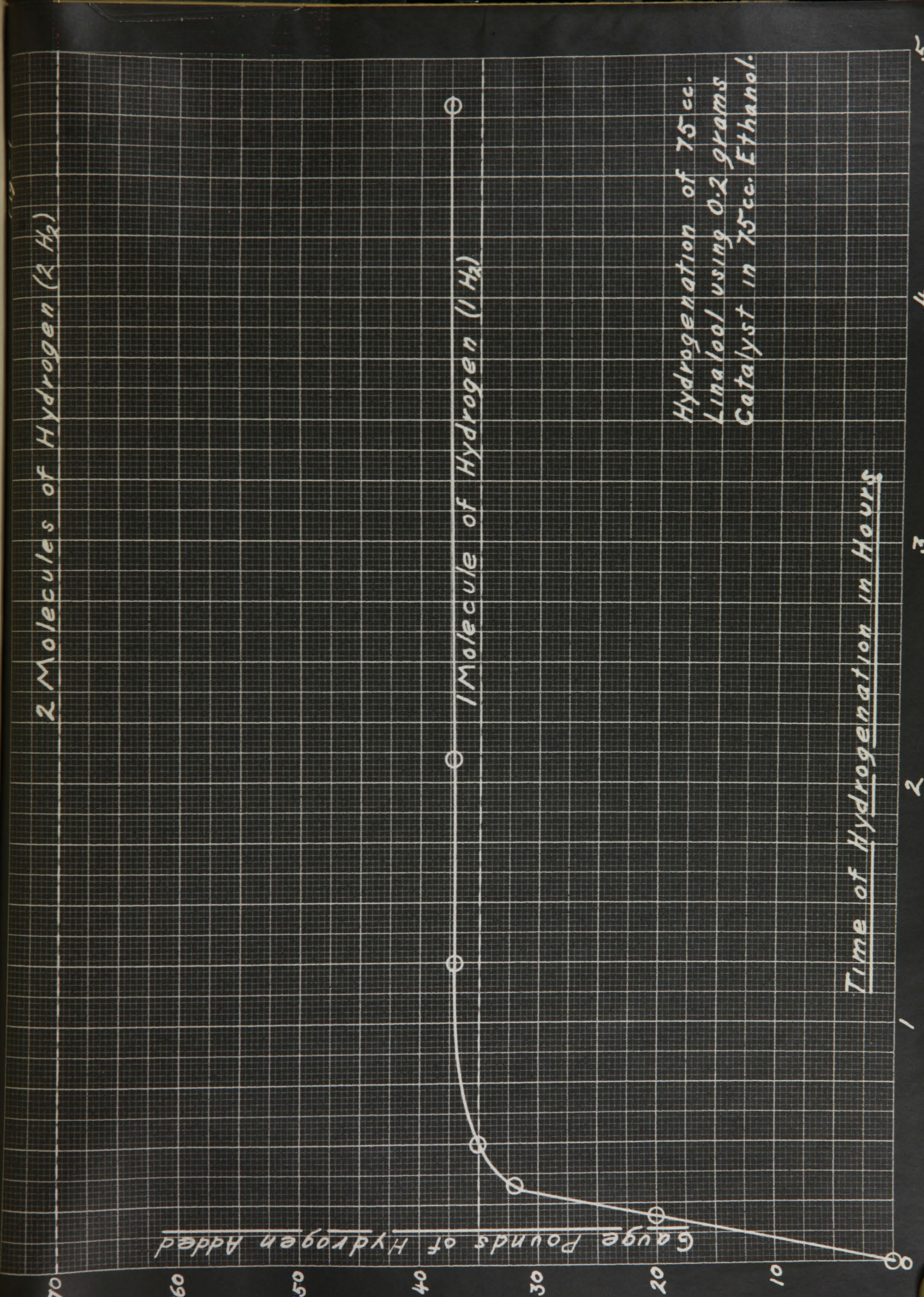
The various fractions had the following properties:-

| Frac. | Tube Length dm. | Temp. °C. | $\alpha_D$ | $[\alpha]_D$ | $(M)_D$ | $d^{25}_{4}$ | $N^{25}_{D}$ | M.R. Calc. | M.R. Found |
|---|---|---|---|---|---|---|---|---|---|
| 1 | - | - | - | - | - | - | 1.4347 | - | - |
| 2 | 1 | 25 | -0.09 | -0.10 | -0.18 | 0.8647 | 1.4348 | 53.25 | 53.28 |
| Residue | - | - | - | - | - | - | 1.4348 | - | - |

None of the above fractions showed unsaturation on testing with a solution of bromine in glacial acetic acid.

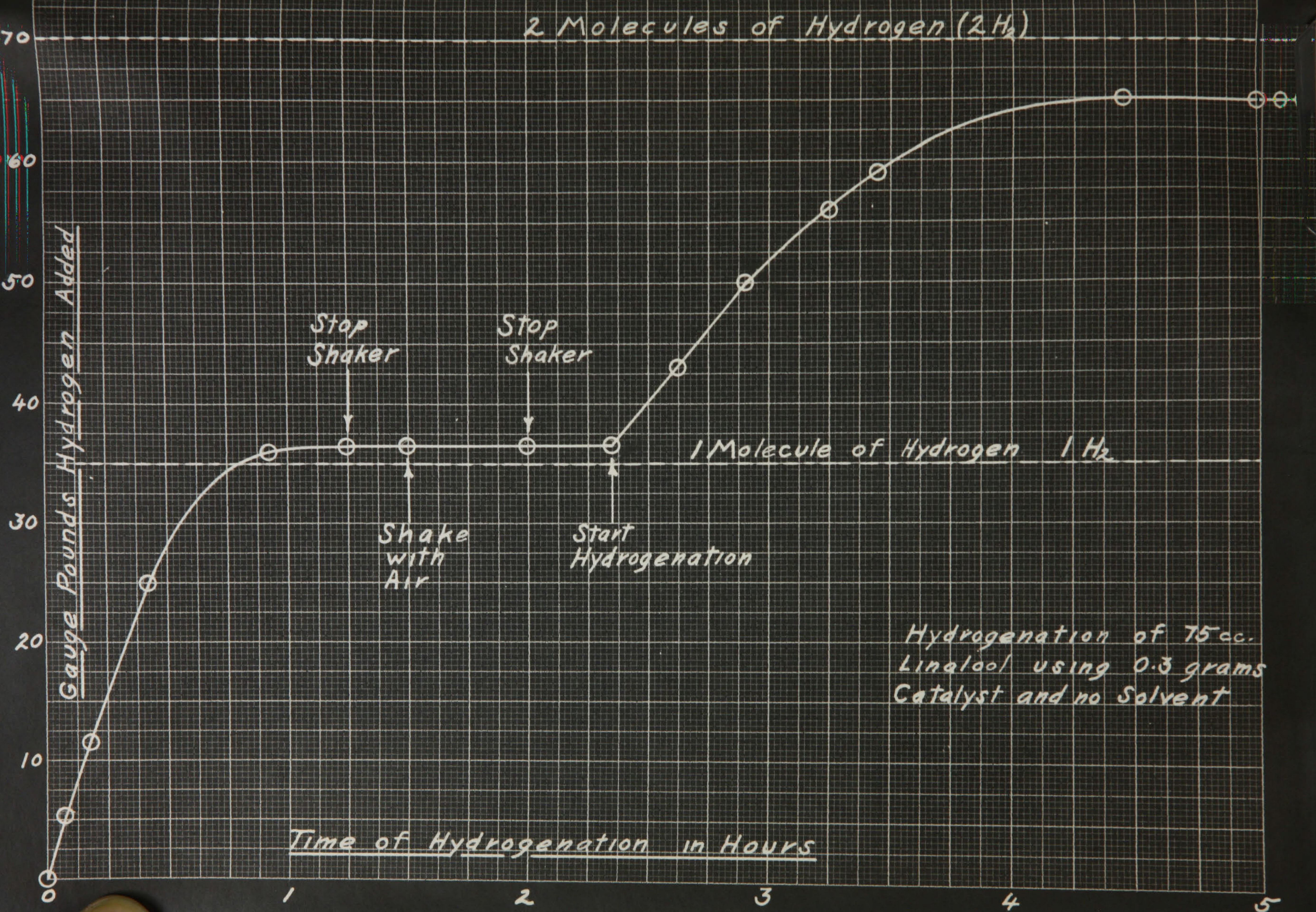
Fraction 2 was analyzed for total chlorine content with the following results:-

| Total Chlorine | | | Theoretical Chlorine % |
|---|---|---|---|
| Sample Weight gms. | Ag Cl Weight gms. | Chlorine % | |
| 0.6165 | 0.4915 | 19.8 | 20.1 |



Hydrogenation of 75 cc. Linalool using 0.2 grams Catalyst in 75cc. Ethanol.

Fig. 2.



Hydrogenation of 75 cc. Linalool using 0.3 grams Catalyst and no Solvent