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CHRYSENE AND DERIVATIVES

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CHRYSENE AND DERIVATIVES

By

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The writer takes this opportunity  
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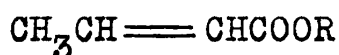
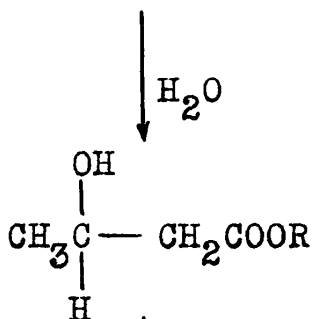
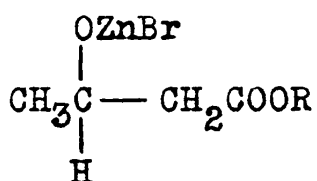
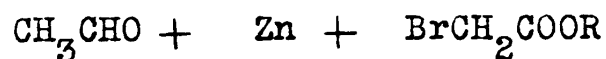
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## Historical

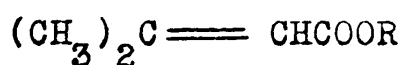
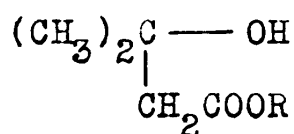
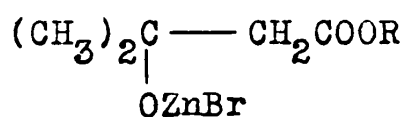
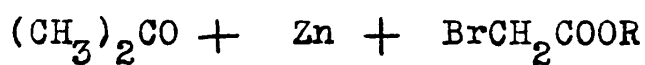
The Reformatsky reaction is essentially a reaction between the carbonyl group in an aldehyde or ketone, an alpha-bromoester and zinc, using dry benzene as solvent. Thus, in the first example below, acetaldehyde, the bromoacetic ester and zinc give rise to an addition product which is analogous to the addition product of the Grignard reaction. This on hydrolysis gives the beta-hydroxyester which easily loses water on heating to give an alpha,beta-unsaturated ester.

### Example I



Likewise, in the second example, the ketone, acetone, behaves in a similar manner as shown by the parallel reactions.

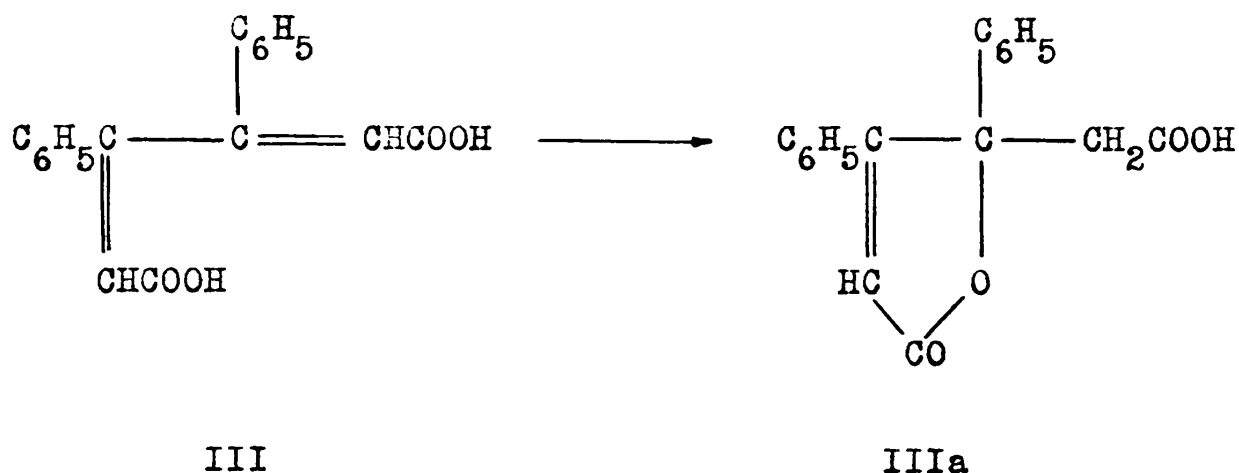
Example II



Incidentally, the reaction is important in the preparation of alpha,beta-unsaturated esters and acids.

In 1911, Beschke (1) described the synthesis of chrysene using, as his initial reaction, the Reformatsky reaction described above. In this synthesis, the carbonyl compound was the diketone benzil and the ester, ethyl bromoacetate. The reaction product consisted of two isomers, cis and trans  $\beta,\beta$ -dihydroxy- $\beta,\beta$ -diphenyl adipate I; the trans

isomer eventually leading to his synthesis of 2,8- or amphi-chrysenequinone which will be dealt with in the present paper. The trans form of the ester was dehydrated with acetic anhydride and concentrated sulphuric acid and the resultant lactone II hydrolysed with sodium hydroxide to give the sodium salt of the diphenylmuconic acid III. On acidification, the highly unstable free acid lactonized immediately to its isomer IIIa.

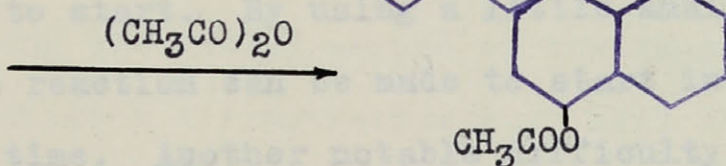
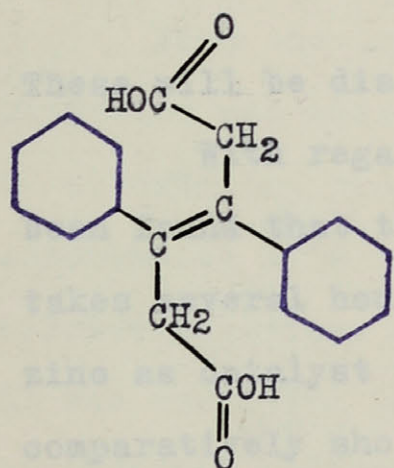
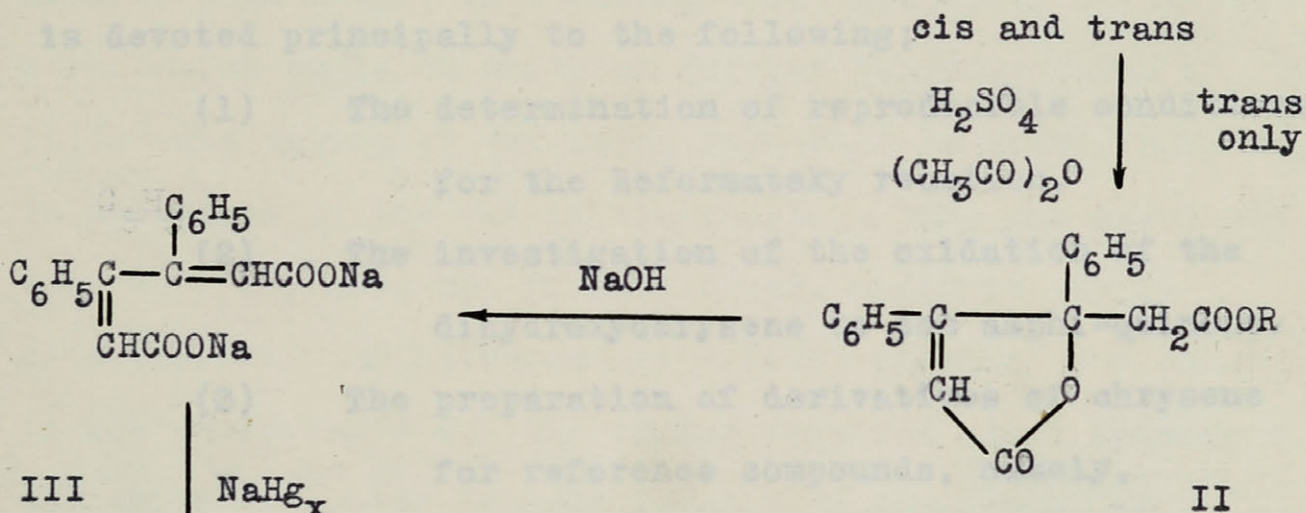
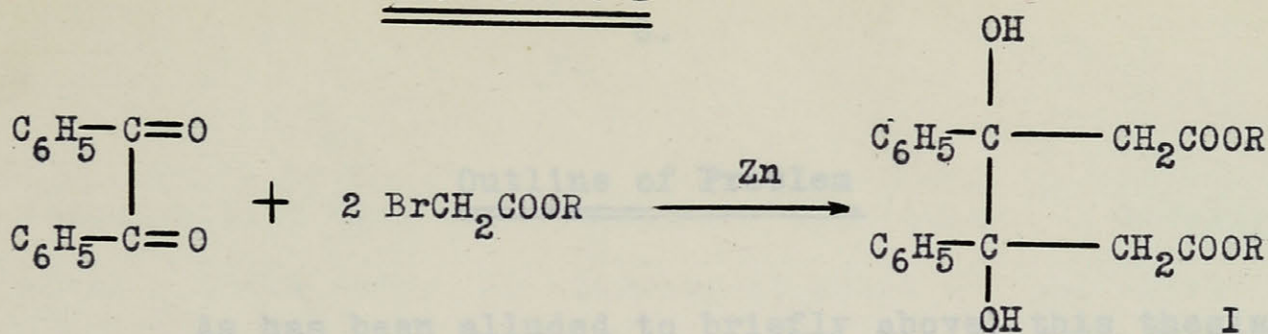


This lactone ring, however, is reopened when the acid is dissolved in sodium hydroxide prior to the next step in the synthesis which is reduction with sodium amalgam (3). Upon reduction the diphenyl-dihydromuconic acid IV was formed and this, by means of acetic anhydride and concentrated sulphuric acid underwent ring closure to form diacetoxychrysene V. In the next step, the acetyl groups were hydrolysed off by alcoholic sulphuric

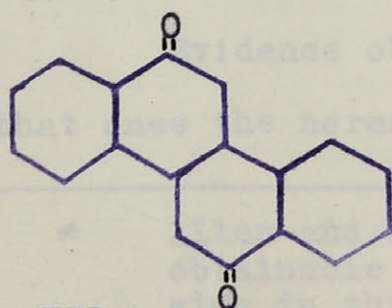
acid to give the dihydroxychrysene VI and this was subsequently oxidized with lead peroxide to the desired 2,8- or amphi-chrysenequinone. The reactions described are summarized in Flow sheet I.

In our detailed study of the synthesis, results disclosed a number of difficulties encountered in the Reformatsky reaction and a serious irregularity in the last step in the oxidation to the quinone. A compound, also a quinone, always appeared in the oxidation product as a contaminant but no mention of it was made in the original literature. Attempts were made, therefore, to determine the optimum conditions for securing the amphi-chrysenequinone in good yield. In the following section we have presented a description of the work dealing with the Reformatsky reaction, the intermediate steps and the final oxidation. The evidence which ultimately led us to a method of securing the 2,8- or amphi-chrysenequinone in satisfactory yield will be fully described.

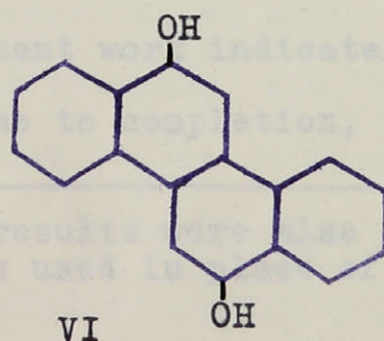
Flow sheet I



alc. H<sub>2</sub>SO<sub>4</sub>



PbO<sub>2</sub>



Outline of Problem

As has been alluded to briefly above, this thesis is devoted principally to the following;

- (1) The determination of reproducible conditions for the Reformatsky reaction.
- (2) The investigation of the oxidation of the dihydroxychrysene to the amphi-quinone.
- (3) The preparation of derivatives of chrysene for reference compounds, namely, 8-hydroxy-1,2-chrysenequinone and its acetate and quinoxaline.

These will be discussed in order.

With regard to the Reformatsky reaction,<sup>\*</sup> it has been found that the reaction, when not catalysed, generally takes several hours to start. By using a little amalgamated zinc as catalyst the reaction can be made to start in a comparatively short time. Another notable difficulty was experienced in the separation of the reaction product in a solid state. This was obviated, as described in the work of Allen and Gilman (2) by recourse to iced sulphuric acid.

Evidence obtained in the present work indicates that once the normal reaction has gone to completion, the

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\* Allen and Gilman found that results were also obtainable when magnesium was used in place of the zinc in this reaction.

7.

decomposition does not present any difficulty; it invariably gives a solid ester. On stirring at about  $0^{\circ}$ , the ester hardens into lumps; on standing these gradually soften to a yellowish emulsion which on further standing forms a solid cake on top of the acid. Care must be taken, however, to ascertain at the end of the reaction that the ester has been entirely used up. If some ester, which is easily detectable by its lachrymatory effect, remains, the solid is not as workable and the drying requires added attention, the extent of which depends largely on the amount of unreacted bromoacetate.

From the trial runs made, it was found that when the bromester was added slowly at the beginning it was possible to observe the reaction point; a vigorous reaction set in accompanied by a change from a yellowish to a brownish colored solution. During the entire period of the reaction it was essential to maintain a temperature such that the mixture was boiling briskly under rapid stirring.

The amount of benzene used as solvent is also important. It has been observed that when insufficient benzene is used the reaction product separates as a resinous mass in the reaction flask and the zinc, some of which always remains, becomes so imbedded in the product that one runs into difficulty. On the other hand, when sufficient benzene is used, the suspension of yellow product

obtained at the end of the reaction can easily be poured out and the zinc, by virtue of its greater density, remains behind, thus affording a very clean separation. If protected from moisture, the flask containing the zinc can be used directly for subsequent runs and any loss of material thereby avoided.

It must be mentioned, too, in connection with the reaction product, that if an appreciable amount of unremoved zinc is in contact with the acid, a reduction takes place. This was noticed in the case of methyl bromoacetate, where the reaction product turned red on standing.

In the dehydration of the ester, it was found advantageous to use dry benzene first to remove as much as possible of the water mechanically retained. After the benzene was completely removed under vacuum, acetic anhydride was added to perform the dehydration which resulted in the lactonization.

At this point mention must be made of the work that was done with methyl bromoacetate. From many runs, the results obtained led to the conclusion that the Reformatsky reaction does not give a satisfactory product in this particular instance with the methyl ester. Carefully distilled fractions of the bromoacetate were used and all led to poor results; this eliminated the possibility that it was due to the quality of the ester. On the other hand, ethyl bromoacetate fractions of fairly wide b.p. range have been used and gave



results comparable to those in which fractions of small range had been used. Also, the acid decomposition product was in most cases too oily to work easily with. Upon dehydration with acetic anhydride and concentrated sulphuric acid, and subsequent decomposition in iced sodium carbonate solution, only an oily material was obtained. The crude ester resulting from the acid decomposition gave a white crystalline product, m.p. 200-2° after recrystallizing five times from methyl alcohol.

The sodium carbonate decomposition product from the ethyl bromoacetate is invariably an unfilterable gummy solid. At ordinary temperature, the material is too fluid and decantation of washings resulted in loss of material. To obviate this difficulty, the washing was done with iced water; this caused the material to remain as a firm mass in the bottom while the washing liquid was decanted. After the bulk of the material was transferred to the flask for hydrolysis, the remaining material was rinsed over with a little dilute sodium hydroxide.

It was found that the hydrolysis with 10% sodium hydroxide was best continued for three hours; two hours resulted in an incomplete hydrolysis as shown by the fact that the residue yielded more material on repeating the operation. Decolorizing charcoal was added and the heating continued for another 15 minutes after which time the

solution was filtered by suction.

In the precipitation of the desired trans 1,4-diphenylmuconic acid, best results were obtained when the above solution containing the corresponding sodium salt was diluted and well-cooled in ice and then dilute hydrochloric acid (also cooled in ice) added slowly with thorough stirring. The buff coloured acid was filtered, dissolved in the least amount of 10% sodium hydroxide, and filtered through decolorizing charcoal. After dilution to three times its volume and again cooling in ice, the acid was reprecipitated as before. After filtration the acid was a uniform buff colored product; m.p. 170-1<sup>o</sup>. Filtration by suction through a one-quarter inch matting of charcoal as mentioned above has been found to be very effective in this stage of the work.

In the reduction of the above acid with sodium amalgam it has been found that results fully justified the reprecipitation. With reprecipitated acid, the reduction product was white; it had a m.p. of 285<sup>o</sup> and it was satisfactory without digesting in alcohol whereas the acid that was not reprecipitated gave a slightly yellowish acid having a lower m.p. of 270-8<sup>o</sup>.

In the ring closure to give the diacetate it was observed at first that the diphenyl-dihydromuconic acid did not all dissolve but that some particles of it always

remain after standing two hours as the original directions called for. Later it was found that if the acid was broken up finely and the whole mixture allowed to stand, not two hours, but four to five hours in cold water, the acid dissolved in entirety. Under these conditions the crystalline needles were much longer and heavier.

The hydrolysis of the diacetate with alcoholic sulphuric acid was found to give a product that gave little in the way of result. Subsequent investigation brought to light the fact that the quality of the hydrolysis product was dependent on the solvent that was used. The importance of this development will become evident when the following discussion is taken up.

The intermediate steps of the synthesis described above introduces the last and by far the more unsatisfactory phase of the problem. This is the oxidation of the dihydroxychrysene with lead dioxide to the quinone. The inadequate directions given in Beschke's work did not divulge the actual conditions necessary for this step. In the experiments that follow we will first give a full description of the work done on one lot of diol which consisted of material obtained from three preparations carefully made under identical conditions throughout. In every case, the oxidation resulted in a negligible yield of amphi-chrysenequinone and a large yield of a red compound,

also a quinone and which was not reported in the literature. Allen and Gilman, who isolated this compound, had concluded that it was an ortho-quinone since it gave a quinoxaline with o-phenylenediamine. It was surmised that it might be a hydroxyquinone in which case it would be reasonable to assume that the oxidation had gone too far. By varying the time it was found that over four minutes and not above eight minutes heating during oxidation gave the best yield of crude material from which the amphi-quinone was isolated by recrystallization from acetic acid. By varying the amount of acetic acid used as solvent in the oxidation it was found that 80 cc. per gram sample was satisfactory; beyond this amount, the material required a longer time to deposit and was invariably accompanied by a large quantity of the red quinone. With regard to the temperature, results obtained between 105-110° showed no divergence from those obtained at ±99°. Reproducible results were obtained in the 100-110° range.

Several observations have been made in connection with the use of the oxidizing agent. Best results were obtained when the lead dioxide, ground fine in a mortar, was added in small portions to the suspension of diol in acetic acid with thorough stirring after each addition. At the end of the heating any unused particles of dioxide remaining in the solution were filtered and the filtrate

allowed to stand.

Evidence will be presented herewith to show the line of reasoning we adopted in an effort to reach our objective, namely, to secure ultimately, optimum conditions for an experiment which will give us a satisfactory yield of the desired amphichrysenequinone. At the outset, we proposed to determine if the red ortho-quinone was **unmistakably** an oxidation product due to excessive oxidation. Several experiments were performed and the checked results provided us with an adequate answer to this question. The red quinone definitely did not come from the amphiquinone. By another set of experiments, we also satisfied ourselves that the red quinone did not yield any amphiquinone in the lead dioxide treatment, a result that we anticipated but which we wanted appropriate evidence to vouch for.

Following our investigation on the lead dioxide treatment, our attention turned to the preparation of the diol itself. It was considered as possible that the quality of the product in our case had an influence on the course of the reaction during oxidation. Experiments carried out based on this line of reasoning led us to discover the importance of the solvent used in the hydrolysis.

In one particular preparation, the mother liquor

from a previous hydrolysis was used after a reddish deposit that had settled at the bottom of the flask was filtered. The hydrolysis was then carried out as in the other cases. When the product was filtered and washed with hot acetic acid, it was found to be different from previous preparations. Not only did it differ in colour, crystalline form and melting point but most important of all, in its behaviour with lead dioxide; it gave the amphi-quinone free from the red quinone upon treatment with the oxidizing agent.

Thus the procedure that first proved successful for securing a good quality of the diol involved using the mother liquor from one run as solvent for the next. The reason for the superiority of this solution over the solvent seemed to be connected with the presence of some impurity (perhaps acetaldehyde) in the alcohol. At any rate, carefully prepared aldehyde-free alcohol proved satisfactory and gave excellent results. The evidence that we have been able to obtain showed very clearly that the chief difficulty experienced in getting the amphi-quinone was due to the inferior quality of the diol available.

Upon close examination of the reddish solvent deposit under the microscope, the red part was found to be heterogeneous; it was composed of bright red crystals

on a dull red substance. Unfortunately, the time available did not permit a complete study of this phase of the work. We have isolated, however, the dull red substance and found that a sample recrystallized from acetic acid decomposed above 300° and that it formed a quinoxaline with o-phenylenediamine.

For reference purposes, 8-hydroxy-1,2-chrysenequinone, its acetate and quinoxaline were prepared.

ExperimentalEthyl bromoacetate

\*

To 100 g. of glacial acetic acid and 4 g. acetic anhydride heated to boiling in a flask with a ground-glass connection and fitted with a reflux condenser-absorption bottle arrangement was added 35 g. bromine by an addition side arm. When the vigorous reaction subsided, a further 231 g. of bromine was added in small portions. The mixture was refluxed gently for one hour, then heating stopped. In the same apparatus, the brownish  $\alpha$ -bromoacetic acid was esterified with 225 cc. distilled ethyl alcohol added through the side arm. After two hours refluxing, the ethyl bromoacetate was poured into cold water. The ester layer was separated, washed twice by decantation with water and then dried over  $\text{CaCl}_2$ . It was then transferred to a distilling flask with a ground-glass connection and the fraction of b.p. 157-162° was collected. The product was water-white; the yield was 216 g. or 78%.

Notes

1. During the bromination, the volatile compound  $(\text{CH}_3\text{COOH}\cdot\text{Br}_2)_4\text{HBr}$  (5) caused frequent choking of

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\* Commercial acetic acid was partially frozen in an ice bath and after the liquid portion decanted, the crystals, after thawing, were used.



the condenser. It has been found since that the difficulty could be avoided by using red phosphorous with the bromine according to a procedure in Organic Syntheses (6).

2. The yield of ester has been observed to improve when the esterification was continued for a half hour longer than the time specified.

### Methyl bromoacetate

To 232 g. of the brominated acetic acid prepared by the above method, 225 cc. of methyl alcohol and 1-2 cc. of constant boiling HBr were added. The esterification and the subsequent separation and washing of the ester were carried out in a manner identical to the procedure described above for the ethyl bromoester.

From several preparations, the following fractions were collected for the work to be described in the Reformatsky reaction; b.p. 140-150°, 142-148°, 145-147°, 145-150°. The first fraction corresponded to an 80% yield.

### Reformatsky reaction

To 11 g. of benzil, 11 g. of zinc turnings (cut specially for this reaction from C.P. Baker sticks Lot No. 101524) in a 1000 cc. 3-neck flask was added 50 cc. dry benzene. The flask was then fitted with 2 Friedrich

condensers, a dropping funnel and a mechanical stirrer. Next were added: a few pieces of zinc amalgam prepared by touching the zinc quickly to a small portion of clean mercury that has been wetted with a drop of concentrated  $\text{H}_2\text{SO}_4$  and the mixture was brought to boiling over a steam bath. To the briskly boiling yellow mixture was then added dropwise 20 g. of the ethyl bromoacetate. In a short time (when about 80% of the ester has been added) a vigorous reaction set in and the mixture turned brown. (The addition was regulated so that all the ester was added during the first 20 minutes). After an hour of refluxing with the temperature maintained at the brisk boiling point, the heating was discontinued and the contents of the flask allowed to cool. At this stage, the unused zinc appeared finely divided; this has been observed to be a valuable indicator at the end of the reaction. The liquid part was poured into iced  $\text{H}_2\text{SO}_4$  and well stirred to ensure a thorough decomposition. Yellow lumps were first formed; these on standing soften to an emulsion and this, on standing overnight, formed a solid cake on top of the acid. The solid ester was removed and dried on a porous plate. The crude ester weighed 16 g., or a yield of 70%.

#### Dehydration and decomposition of the ester I

To 16 g. of the crude ester in a distilling flask,

30-40 cc. of dry benzene was added. After a few pieces of porous plate were introduced and the distilling arm connected with the suction, the flask was set in a water bath 40-50° and the benzene together with the water it had taken up was removed under vacuum. To the ester thus treated was added 50 cc. of acetic anhydride followed by 3 cc. conc. sulphuric acid. The mixture turned green accompanied by considerable evolution of heat. After cooling under the tap, the contents were slowly poured into iced sodium carbonate solution and well stirred. From this decomposition, a reddish brown layer of gummy material was formed, which, on standing, settled to the bottom. After the liquid was decanted, two portions of ice water were added, stirring well after each addition, and the washings decanted. The bulk of the material was then transferred to a 1000 cc. r. b. flask fitted with a reflux column and the remainder rinsed over with some dilute sodium hydroxide.

Hydrolysis of the lactone II and precipitation of  
diphenylmuconic acid

To the above material in the flask, 200 cc. of 10% sodium hydroxide and 50 cc. of water were added and the contents refluxed for three hours. At the end of this time the solution was decolorized with 2 g. of bone charcoal (Mallinckrodt's) and then filtered by suction. After

dilution with an equal amount of water, the solution, now light yellow in color, was cooled in ice to 0-5°. Dilute hydrochloric acid (35%) likewise cooled was added slowly till the solution was acid, thoroughly stirring it all the while to prevent the formation of lumps. At the acid point, the product thrown down was brown in colour.

The precipitate was filtered by suction, dissolved in a minimum amount of 10% sodium hydroxide, diluted to three times its volume and filtered through a one-quarter inch matting of the bone charcoal. The filtered solution, now much lighter in colour, was again cooled in ice and the acid precipitated as before. It was then filtered, washed and dried. The buff-coloured acid obtained had a m.p. of 170-1° and its yield was 9.1 g. or 74%.

#### Reduction of diphenylmuconic acid

In a 500 cc. Erlenmeyer flask, was dissolved in a small quantity of dilute sodium hydroxide 8 g. of the reprecipitated acid and the solution diluted to a volume of 250-300 cc. Sodium amalgam, prepared according to directions given in Org. Syn. (3) and calculated to be in excess over the amount required, was carefully introduced in portions and the solution set aside. The evolution of hydrogen was slight, indicating a normal reduction. On standing 8-9 hours, the reddish colour changed to yellowish. To complete the

reduction, the flask was set in warm water (30-40°) for a half hour. After dilution with one half its volume of water, and cooling to 0-5°, the solution was filtered by gravity into dilute hydrochloric acid that has been cooled in ice water. In this manner, a snow-white acid was precipitated. This was filtered, washed and dried. It gave a yield of 3.9 g. or 48% and it had a m.p. of 285°.

#### Ring closure and formation of the diacetate V

To 8 g. of the finely ground reduced acid was added 50 cc. of acetic anhydride. The mixture was cooled in ice water and 8 cc. of conc. sulphuric acid was added dropwise. On standing the mixture turned brown and became very mushy as was plainly evident during the intermittent shaking. At the end of 4-5 hours standing in the cold water, the product was filtered and washed with acetic acid, ethyl alcohol and finally with a small quantity of ether. When dried the long colorless needles of m.p. 225-30° weighed 7 g. giving a yield of 75%.

#### Hydrolysis of the diacetate to the diol VI

In a 250 cc. 3-neck flask fitted with a dropping funnel, a mechanical stirrer and a reflux condenser was placed 4 g. of the prepared diacetate with 160 cc. of redistilled ethyl alcohol. To this mixture, gently heated on the water

bath, 10 cc. of conc. sulphuric acid was slowly added (preferably) dropwise. The hydrolysis was maintained for two hours and then the refluxing discontinued. The crystalline material was filtered when the contents had cooled, washed with hot acetic acid and then dried as much as possible by suction. The yield of greyish material was 2.3 g. or 76% and the m.p. was 293-300°.

#### Lead dioxide treatment on amphi-chrysenequinone

To a hot solution of 0.1 g. of amphi-chrysenequinone of m.p. 260-75° (sample from Dr. Allen) in 10 cc. of acetic acid was added 0.1 g. of lead dioxide (Baker's C. P. stock) in small portions during intervals. The heating was continued for 40 minutes with frequent stirring and then the solution was filtered hot and allowed to stand. On cooling, the amphi-quinone was deposited. No change was observed after several days' standing; no traces of any red by-product were found. The material was filtered and subjected to the same lead dioxide treatment, this time for one hour and the amphi-chrysenequinone was recovered unchanged to the extent of 0.07 g. after it was allowed to stand several hours.

Note This result has been confirmed by subsequent experiments and it established the fact that the red ortho-quinone does not come from the amphi-chrysenequinone due to oxidation carried too far.

Lead dioxide treatment on the red ortho-quinoneNote

The following result was also obtained in two other experiments one of 30 minutes and the other 45 minutes heating. It confirmed our anticipation that the amphi-quinone could not have come from the ortho-quinone.

To a hot solution containing a 0.06 g. of the scarlet red ortho-quinone, m.p.  $235-6^{\circ}$  (sample from Dr. Allen) in 8 cc. acetic and at a temperature of  $99-100^{\circ}$  was added 0.06 g. lead dioxide. After 10 minutes of heating, the red solution was filtered and left to stand. On cooling, crystals of the red quinone formed immediately; no trace of amphi-quinone was observed. The crystals gave a m.p. of  $236^{\circ}$ .

Oxidation of the diol to the amphi-quinoneNote

The following experiments were carried out to determine the influence of time, volume of acetic acid and temperature on the oxidation. It will be noted that while conditions have been determined to give the best yield of material from which the amphi-quinone can be obtained,

the yield of the amphi-quinone in every case was small. The brown material showed traces of red, the amount of which was observed to depend directly on the length of time the solution was allowed to stand. After filtration, the filtrate invariably gave a deposit of the red quinone when allowed to stand for some time.

Oxidation: 2 minutes

To 0.1 g. of the diol prepared above, suspended in 8 cc. acetic acid and heated to  $100^{\circ}$  was added 0.1 g. lead dioxide in small portions with stirring. After 2 minutes heating, the deep orange coloured solution was filtered and allowed to cool. Some red quinone was deposited in a half hour and which increased in quantity after 1 hour standing. On allowing most of the solvent to evaporate there was found a small amount of amphi-quinone deposited on top of the red quinone.

Oxidation: 4 minutes

In a similar experiment, the heating was continued for 4 minutes. On cooling, the filtrate deposited brownish-yellow material weighing 0.05 g. and which showed traces of red. This material was dissolved in hot acetic acid, again filtered, and allowed to cool. In 5-10 minutes,



yellow material badly spotted with the red quinone was deposited. The material weighed 0.04 g. and it had a m.p. of 185-90°. The filtrate on standing yielded a further deposit of the red quinone.

Oxidation: 8 minutes

In this experiment, the heating was increased to 8 minutes. Similar to the 4 minute one, the large quantity of brownish-yellow material deposited showed red specks uniformly distributed on top of it. This material was filtered and recrystallized from p-cymene. The red quinone came down as fine red particles that adhered to the bottom of the beaker while the amphi-quinone of m.p. 259-68° appeared in lemon-yellow patches on top of them. The quantity of amphi-quinone obtained was very small.

Oxidation: 16 minutes

In still another experiment, the heating was prolonged to 16 minutes. The material deposited in this case was different; it was orange in colour, on the red side. It was filtered and when recrystallized from acetic acid, it consisted of yellow material spotted with the red quinone and bundles of amphi-quinone needles with only traces of red. The needles had a m.p. of 255-63°. The yield of the desired product was again negligible. The

filtrate on standing deposited the red quinone as usual.

Oxidation: 5 cc. solvent

One-tenth gram of the diol was subjected to a 4 minute oxidation as described above, with the amount of acetic acid reduced to 5 cc. Immediately after the filtration, a liberal quantity of the red quinone had already formed. Minute traces of the amphi-quinone were evident on close examination. After one hour, the solution was filtered. The material was mostly of the red one with some amphi-quinone on top of it. On standing, the filtrate deposited a small amount of the amphi-quinone spotted with specks of red.

Oxidation: 10 cc. solvent

The filtrate in this case first deposited fine red particles when allowed to stand for a short time (1-2 hours) and then after one day, a small amount of the amphi-quinone appeared on the red one.

Oxidation: 20 cc. solvent

When a larger quantity of the acetic acid was used, the solution after the usual filtration took from 4 to 5 hours to deposit the red quinone, but, during this period of time, examination revealed that no amphi-quinone had

been deposited. The red quinone obtained in this run gave a m.p. of 232-35°.

Oxidation: 105-110°

In a 0.1 g. sample using 8 cc. of acetic acid, 0.1 g. of lead dioxide and in which the oxidation was continued for 4 minutes, the filtrate deposited the brownish-yellow material described in previous experiments. Traces of orange material were also observed on close examination when the deposit was filtered. Two days later, an orange material was deposited by the filtrate. The brownish-yellow material was dissolved in hot acetic acid, filtered, and allowed to stand. A small amount of amphi-quinone with traces of orange material was obtained.

Oxidation: solvent at boiling point

In a similar run, the oxidation was carried out in boiling acetic acid. Results obtained showed no divergence; they corresponded to those described in the experiment conducted at 105-110°.

Oxidation of the diol: results at 30 and 60 minutes

Note These two experiments were carried out to determine if any amphi-quinone could be obtained when the heating was greatly prolonged. Results described here

convinced us that excessive heating such as was used, was still capable of giving the desired amphi-quinone, though in a small yield.

Oxidation: one-half hour

In an experiment using 0.1 g. of the diol, 0.1 g. of lead dioxide and 8 cc. of acetic acid, the solution was filtered after a half hour oxidation and allowed to stand. The brownish-yellow material was deposited in a few minutes. This was filtered, dissolved in hot acetic acid, again filtered and then allowed to stand. A small amount of the amphi-quinone was deposited in a quarter hour. This was not filtered, however, and the following day, the red quinone had appeared in large quantity to contaminate it. The first filtrate gave the red deposit after standing 15-20 minutes.

Oxidation: one hour

A similar run was made with the oxidation continued for one full hour. The brownish-yellow material again was obtained; this gave a small quantity of the amphi-quinone after recrystallization from acetic acid. The filtrate first gave a deposit of orange material and then the usual red deposit on standing overnight.

Hydrolysis of the diacetate: a different product

Note: On allowing the alcoholic sulphuric solvent used in the previous hydrolysis (diacetate to diol) to stand, a reddish material was deposited. On close examination this was found to consist of bright red crystals on a dull red substance. The clear fluorescent solution thus filtered, was used again in the following experiment. The diol prepared with it was found to be different from previous samples.

To 3 g. of the diacetate, 90 cc. of the recovered solvent was added and the mixture was refluxed for 2 hours on the steam bath and then the heating was discontinued. After 3-4 hours standing, the contents were filtered and washed with hot acetic acid. The light brown product weighed 1.9 g., a yield of 64%. In a capillary tube it shrunk at 340° and liquefied at 357°.

Oxidation: increased yield of the amphi-quinone

One-tenth gram of the above freshly prepared diol was suspended in 8-10 cc. of hot acetic acid and 0.1 g. of lead dioxide was added in portions with stirring after each addition. As the oxidation progressed, the colour changed to a deep orange. After 5-6 minutes heating near boiling the solution was filtered and set aside to cool.

In a very short time, about 3-4 minutes, the amphi-quinone free from red traces was deposited. The golden-yellow needles were filtered and dried. They had a m.p. of 280° and a yield of 0.065 g. or 65%

#### Preparation of aldehyde-free alcohol\*

To 200 cc. of ethyl alcohol in a 1000 cc. Erlenmeyer flask (preferably a cylinder) was added 0.03 g. of silver nitrate (Merck C.P. crystals) dissolved in a small amount of water and the contents were well agitated. Next was added 0.06 g. of potassium hydroxide (Merck C.P. sticks) dissolved in 10cc. of alcohol. The mixture was allowed to stand for a half hour and then it was transferred to a 500 cc. r.b. flask and refluxed for 30 minutes. When cooled sufficiently, the contents were removed to a dry 250 cc. flask and the alcohol was distilled. The amount collected was 180 cc.

#### Work with aldehyde-free alcohol

##### (a) Hydrolysis

To 3 g. of the diacetate in 80 cc. of the aldehyde-free alcohol was slowly added 10 cc. of conc.

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\* This method given by Dunlap (7) involves the precipitation of the silver oxide in the alcohol. The alkaline oxide oxidizes the aldehyde to acetic acid.

sulphuric acid. The hydrolysis was carried out in exactly the same manner as in previous corresponding experiments. The material was filtered and carefully washed with hot acetic acid. The almost colorless product weighed 1.75 g. and it had a m.p. of 348-52<sup>o</sup>.

(b) Oxidation

A 0.5 g. sample of the freshly prepared diol was oxidized with lead dioxide in the usual manner. Upon allowing the filtered solution to stand, the amphi-quinone was deposited in a large quantity. The golden-yellow needles were filtered and dried with suction. The yield was 66% and the material gave a m.p. of 278<sup>o</sup>.

The preparation of derivatives

8-Hydroxy-1,2-chrysenequinone

To 5 g. of the diacetate suspended in 50 cc. of hot alcohol in a 250 cc. Erlenmeyer flask, 20 cc. of 10% sodium hydroxide was added slowly with stirring. The mixture turned dark blue immediately. The flask was then warmed to 50-60<sup>o</sup> and a strong current of air was conducted through the contents by means of a capillary tube. During the oxidation, a black crystalline material was deposited. Dilute hydrochloric acid (30%) was added till the mixture was strongly acid when the hydroxyquinone

separated out as dark red crystals.

To purify this quinone, the material was filtered, washed free from acid and transferred to an Erlenmeyer flask. After 40 cc. of 50% alcohol had been added, the material was macerated and a dilute solution of sodium hydrosulfite (5 g. in 40 cc. water) added in portions with thorough mixing. In a few moments, the light brown hydroquinone was deposited. Addition of more alcohol and warming brought most of the material into solution. After filtration, the warm solution (30-40°) was allowed to stand exposed to air in an evaporating dish. After 6-8 hours, the dark red needles were filtered from the yellow mother liquor. The purified quinone turned black in a capillary tube at about 315°. The literature stated that no melting point was observed up to 300°.

#### 8-Acetyl-1,2-chrysenequinone

A mixture of 2 g. of the crude hydroxyquinone and 25 cc. of acetic anhydride was gently boiled until the material was completely dissolved; this required about 10 minutes. The orange coloured solution was filtered and allowed to stand in a beaker. On cooling, the acetate was deposited in yellow flakes. These were filtered and recrystallized from acetic acid. The golden-yellow needles thus obtained gave a m.p. of 238-9°. The literature gave a m.p. of 252° for this compound.



Quinoxaline of 8-hydroxy-1,2-chrysenequinone

A mixture of 1 g. of the crude hydroxyquinone and 30 cc. of acetic acid was heated and stirred until the material had completely dissolved. To the dark orange solution was added 0.5 g. of o-phenylenediamine in small portions with stirring. The solution became light brown and gradually developed to a deep green colour. After 5 minutes heating, the solution was filtered and allowed to stand. On cooling, the quinoxaline separated out as greenish-yellow plates. After recrystallization from a 2 : 1 mixture of ethyl alcohol and ethyl acetate, the product formed beautiful greenish-yellow crystals having a m.p. of 287-8°.

Summary

1. Experimental data have been obtained on the Reformatsky reaction using ethyl and methyl bromoacetates, benzil, and zinc turnings in dry benzene as solvent. It has been found that a zinc amalgam catalyst is essential.
2. 2,8-Dihydroxychrysene has been prepared in a satisfactory yield. From this an excellent grade of amphi-chrysenequinone has been secured, free from a red ortho-quinone. It has been shown that the red ortho-quinone does not result from the amphi-quinone, due to oxidation having gone too far, nor is it an intermediate product.
3. 8-Hydroxychrysenequinone, its acetate and quinoxaline have been prepared.

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