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A SYNTHESIS OF 3-OXOTETRAHYDRONAPHTHALENE-2-SUCCINIC
ACID AND SOME RELATED SUBSTANCES

By

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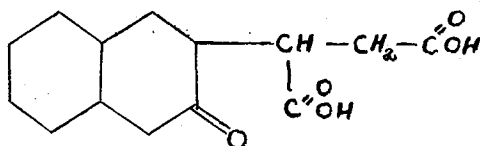
P.G. Olafsson.

AN ATTEMPTED SYNTHESIS OF
3-OXOTETRAHYDRONAPHTHALENE-2-SUCCINIC ACID
AND SOME RELATED SUBSTANCES

INTRODUCTION AND GENERAL SUMMARY:

A synthesis of 2-ketocyclohexylsuccinic acid from cyclohexene oxide was accomplished by McRae, Charlesworth, and Alexander (1). Owing to the similarity between cyclohexene oxide and tetrahydronaphthalene oxide, it seemed probable that the latter oxide would form a similar series of compounds, and it is with a view to determining this that the following work was undertaken.

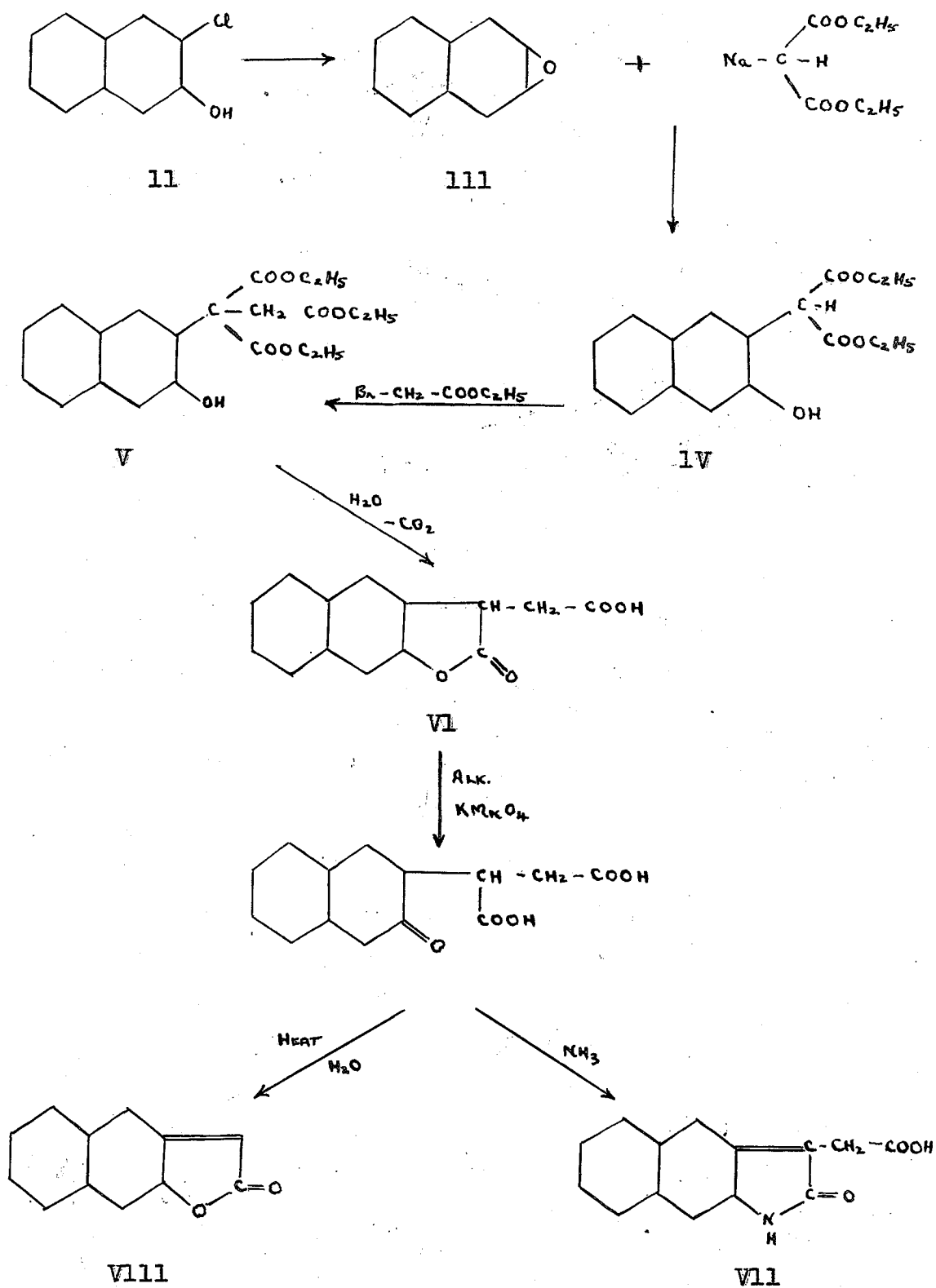
3-oxotetrahydronaphthalene-2-succinic acid (1) may be



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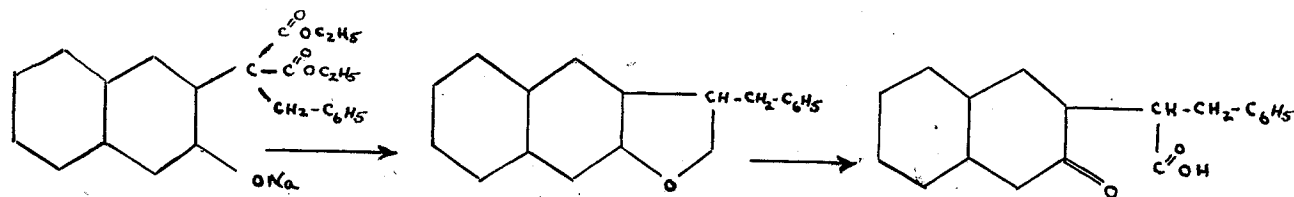
synthesised from 1,4-dihydronaphthalene, which is prepared by the reduction of naphthalene with sodium and absolute alcohol or by the controlled catalytic reduction of naphthalene.

1,4-dihydronaphthalene is reported (46) to react with hypochlorous acid to yield the corresponding chlorohydrin (11), which on addition of base is converted to tetrahydronaphthalene oxide (111).



As tetrahydronaphthalene oxide resembles ethylene oxide in structure, it might be expected to condense with the sodio-derivative of malonic ester and ethyl bromoacetate to yield the tricarboxylic ester (V). Hydrolysis of this ester followed by decarboxylation would probably lead to the formation of the lactone of 3-hydroxytetrahydronaphthalene-2-succinic acid (VI). The oxidation of the lactone by alkaline permanganate or by bromine in the presence of magnesium hydroxide should split the lactone ring in such a way as to yield 3-oxotetrahydronaphthalene-2-succinic acid (I) which, on treatment with alcoholic ammonia might give rise to the lactam (VII). On the other hand, heating the keto acid in vacuo at 200° C would probably result in the loss of one mole of water with the consequent formation of the unsaturated lactone (VIII).

It seems probable that alkyl side chains might be introduced into the 3-position by replacing the β -halogenated ester in the initial condensation by alkyl halides or benzyl chloride.

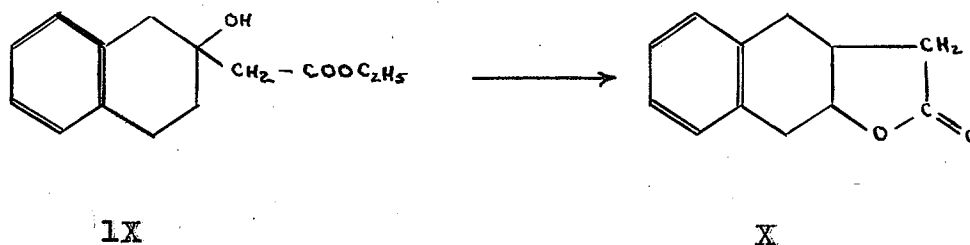


Theoretically 3-oxotetrahydronaphthalene-2-succinic acid may be synthesised using monoketotetrahydronaphthalene as the starting material. The latter is prepared by mixing tetrahydronaphthalene chlorohydrin with two, to two and one half, times its weight of quinoline and heating the mixture in a retort placed over an oil bath. A brownish yellow liquid distills

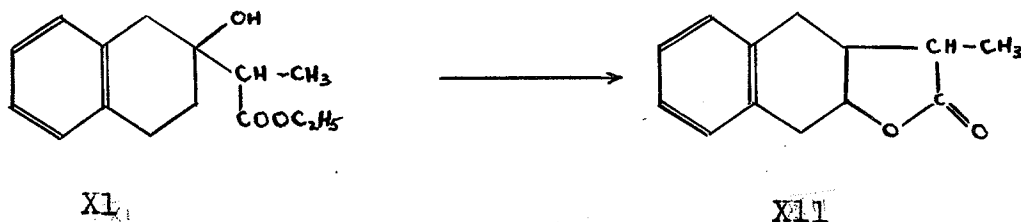
over about 225° C. Once the distillation is complete, the material remaining in the retort is steam distilled. The condensate is treated with sulfuric acid and then extracted with ether. The ether is distilled off and the resulting product treated with sodium bisulfite thus converting the ketone into a bisulfite complex, which may be purified by extracting any organic impurities with ether. On heating the complex with dilute sulfuric acid, the complex breaks down and a brownish oil separates out, which, when distilled under reduced pressure, yields the desired monoketotetrahydronaphthalene.

On the basis of similar work carried out by Charlesworth, McRae, and co-workers on cyclohexene and cyclohexanone, it would seem probable that 3-oxotetrahydronaphthalene-2-succinic acid could be more readily prepared from tetrahydronaphthalene oxide than from monoketotetrahydronaphthalene.

Reformatsky reactions with α -halogenated esters are fairly common. Therefore a reaction involving monoketotetrahydronaphthalene, ethyl bromoacetate and zinc would be expected to yield the hydroxy ester (IX) and on treatment with mineral acid, result in the formation of the γ -lactone (X).

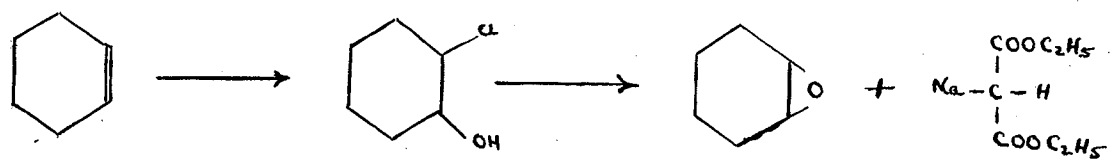


Similarly, monoketotetrahydronaphthalene, ethyl- α -bromopropionate and zinc would be expected to yield the hydroxy ester and, subsequently, the γ -lactone.



Although Reformatsky reactions with α -halogenated esters of monocarboxylic acids are fairly common, there appear to be only two recorded cases of the use of α -halogenated esters of dibasic acids in this reaction. In both cases, the esters of bromomalonic acid were employed. In the case of cyclohexanone, it was found that a Reformatsky reaction would not occur with bromomalonic ester or with ethyl monobromosuccinate. It was concluded that the zinc complex would not react with cyclohexanone to any appreciable extent. There is little hope that it would be more reactive with monoketotetrahydronaphthalene. The failure of condensations involving 2-bromocyclohexanone and the sodio-derivative of esters, as well as that of ethyl cyclohexanone-2-carboxylate and monobromosuccinic ester, lead to a similar conclusion.

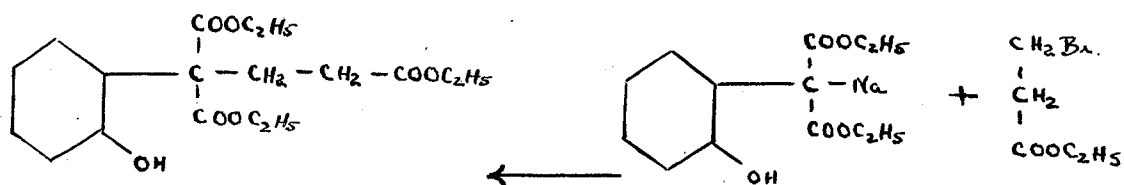
The work of McRae and colleagues (1) centered around the compound α -2-ketocyclohexylglutaric acid and its anhydro and its indole derivatives. This acid had been synthesized by Kendall and Osterberg (2) and the preparation may be represented schematically as follows:-



XI

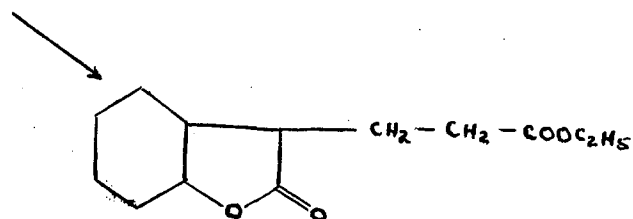
XIV

XV

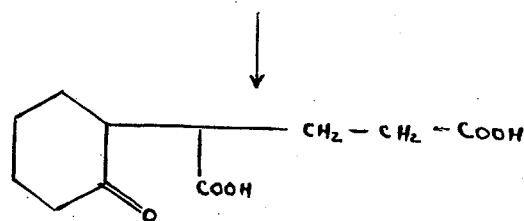


XVII

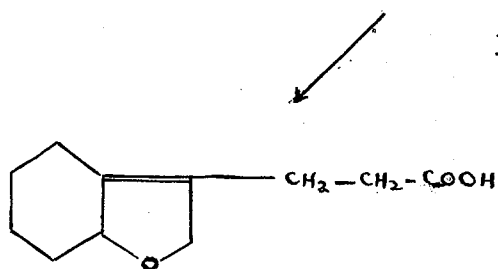
XVI



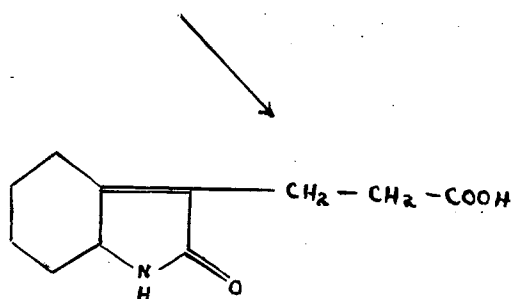
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XIX



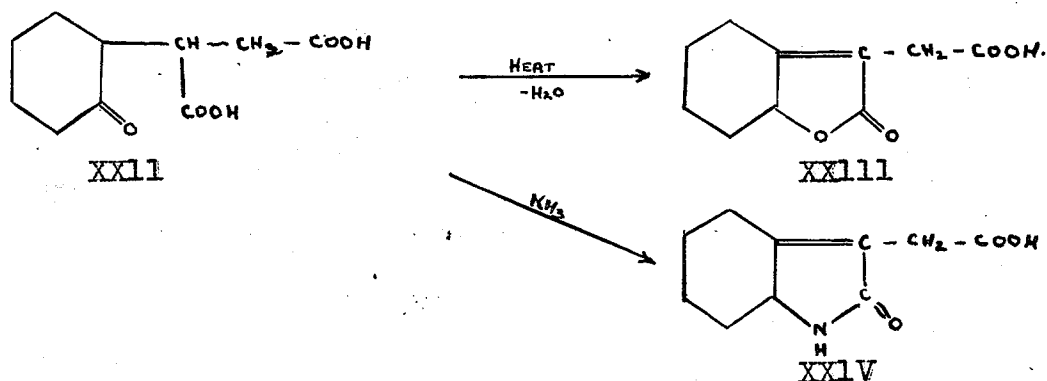
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XXI

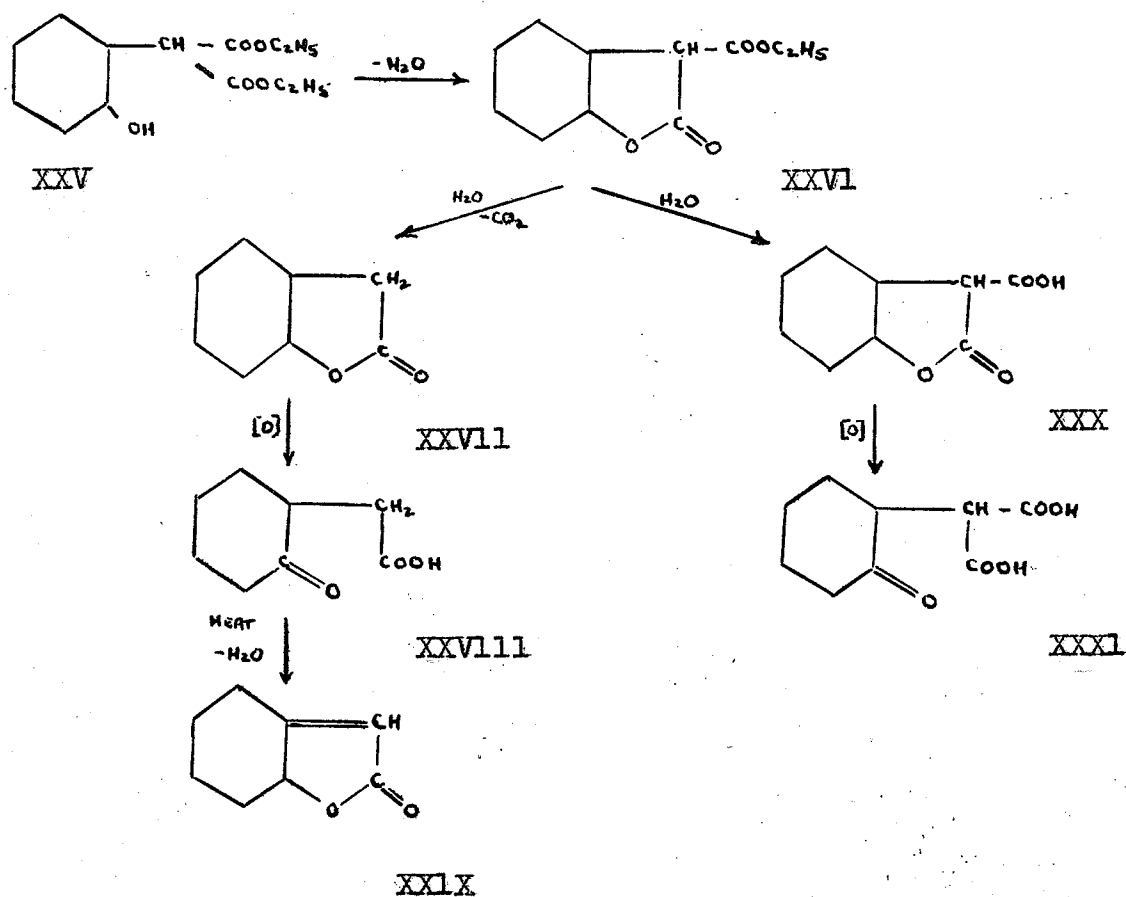
Cyclohexene (XIII) on treatment with a solution of hypochlorous acid yielded the chlorohydrin (XIV) which was converted to cyclohexene oxide (XV) by splitting off the elements of hydrochloric acid in alkaline medium. Through the addition of sodio-activated malonic ester to cyclohexene oxide (XV), the sodium derivative (XVI) was obtained. Elimination of sodium bromide from this compound and β -bromopropionic ester yielded the tricarboxylic ester (XVII) which, on hydrolysis, gave the dicarboxylic lactone and on the loss of carbon dioxide, yielded the glutaric lactone (XVIII). By means of an unusual oxidizing agent, bromine in the presence of magnesium hydroxide, this lactone (XVIII) was converted to the corresponding keto acid (XIX). Two important derivatives of this compound were prepared; the lactone (XX) and the lactam (XXI), the latter being obtained by heating the keto acid (XIX) under pressure in the alcoholic ammonia solution while the former was produced when the keto acid was heated under reduced pressure.

McRae, Charlesworth, and Alexander (1) extended this method to the preparation of other ketocyclohexyl acids and their corresponding lactams. 2-Ketocyclohexylsuccinic acid (XXII) was obtained by condensing cyclohexene oxide with the sodio-derivative of malonic ester and ethyl bromoacetate, the rest of the treatment being identical with that above.



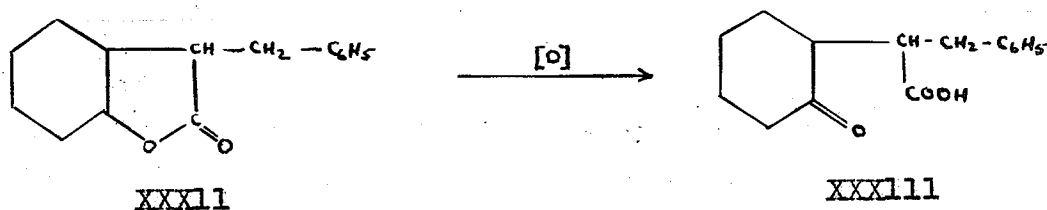
On heating in vacuo at 200° C a molecule of water was lost and the unsaturated lactone (XXIII) was produced. When the keto acid (XXII) was treated with alcoholic ammonia under pressure the lactam (XXIV) was produced.

Coffey (3) condensed cyclohexene oxide with ethyl sodium malonate and obtained the ester lactone (XXVI) which on hydrolysis and decarboxylation yielded cyclohexanolacetic acid lactone (XXVII). By oxidation of this lactone with bromine and magnesium hydroxide, McRae, Charlesworth, and Alexander (1) obtained 2-ketocyclohexylacetic acid (XXVIII). On dehydration, this gave the anhydro derivative which must have had the unsaturated lactone structure (XXIX). They felt it probable that a lactam of (XXVIII) was produced by treatment with alcoholic ammonia, but it was so unstable that it decomposed on attempts at purification.

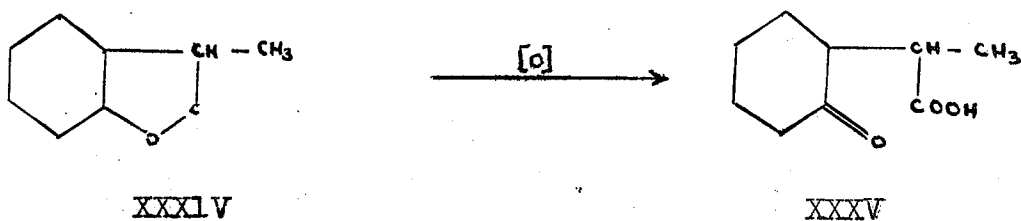


Treatment of the hydrolysed ester lactone (XXX) with bromine and magnesium hydroxide or by alkaline permanganate yielded 2-keto-cyclohexylmalonic acid (XXXI). This acid was rather unstable and tended to decompose with loss of carbon dioxide at the melting point.

McRae, Charlesworth, and Alexander (1) obtained the lactone of cyclohexanolbenzylacetic acid (XXXII) by condensation of cyclohexene oxide, the sodio-derivative of malonic ester and benzyl chloride followed by hydrolysis and decarboxylation. They found that, whereas condensations involving β -bromopropionic ester or bromoacetic ester occurred at room temperature, those involving benzyl chloride or alkyl halides required many hours of refluxing. When (XXXII) was oxidized in the usual way, 2-keto-cyclohexylbenzylacetic acid (XXXIII) was produced. On distillation, this compound lost water and was therefore best isolated in the form of its unsaturated lactone.



When methyl iodide replaced benzyl chloride in the latter condensation, the γ -lactone of cyclohexanol- α -propionic acid (XXXIV) was obtained, which on oxidation with bromine and magnesium hydroxide produced 2-ketocyclohexyl- α -propionic acid (XXXV).

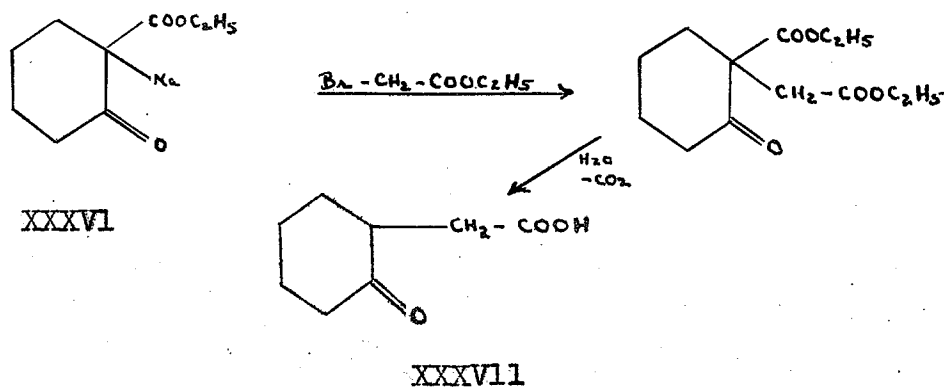


As the synthesis of 2-ketocyclohexylsuccinic acid and related substances from cyclohexene oxide are somewhat involved, Charlesworth, McRae, and MacFarlane (7), in search for simpler methods, and also to confirm the structures assigned, began synthetical work using cyclohexanone as the starting material. Three methods seemed possible.

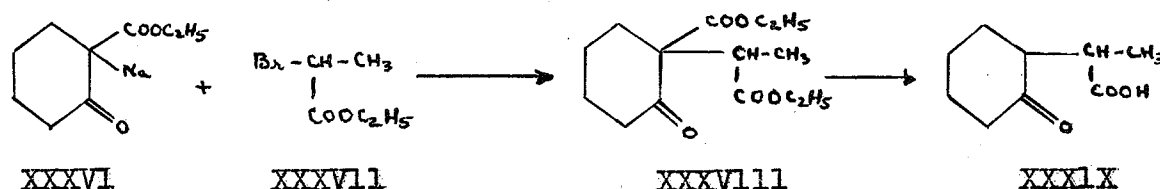
- (1) The elimination of sodium bromide between the sodio-derivative of ethyl cyclohexanone-2-carboxylate and brominated esters, followed by hydrolysis.
- (2) The oxidation of γ -lactones of cyclohexanol carboxylic acids which are prepared by Reformatsky reactions between cyclohexanone and α -brominated esters, followed by treatment with mineral acid.
- (3) The condensation of 2-bromocyclohexanone with the sodio-derivative of the proper substituted malonic ester.

METHOD (1)

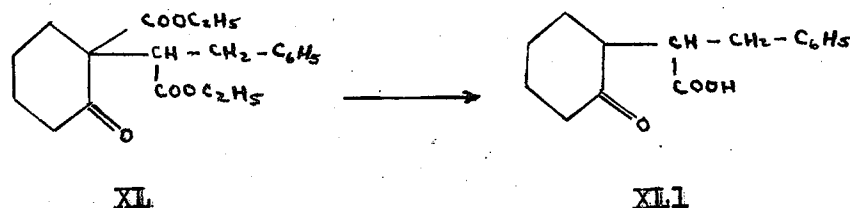
Chuang and Ma (4), Chatterjee (5), and Ghosh (6) synthesised 2-ketocyclohexylacetic acid (XXXVII) from the sodio-derivative of ethyl cyclohexanone-2-carboxylate (XXXVI) and ethyl chloroacetate. Charlesworth and co-workers (7) repeated this preparation, employing ethyl bromoacetate, and obtained a purer product than that prepared by other authors or previously by themselves.



This method was employed by Openshaw and Robinson (8) and by Haworth and Mavin (9). A synthesis of the corresponding 2-ketocyclohexyl- α -propionic acid (XXXIX) resulted when the sodio-derivative of ethyl cyclohexanone-2-carboxylate (XXXVI) was condensed with ethyl α -bromopropionate and the resulting ester (XXXVIII) subjected to hydrolysis.



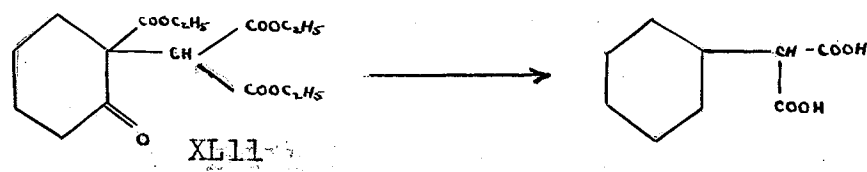
In an attempt to prepare the lactones of cyclohexanolbenzylacetic acid and 2-ketocyclohexylbenzylacetic acid by Method (1), McRae, Charlesworth, and MacFarlane (7) condensed the sodio-derivative (XXXVI) with ethyl α -bromo- β -phenylpropionate, expecting the ester (XL), and on hydrolysis 2-ketocyclohexyl- β -phenylpropionic acid (XLI).



The oil resulting from the condensation had a composition in fair agreement with that of the ester (XL) but molecular weight determination and the production of cinnamic acid from it by the action mineral acid proved it to be ethyl α -hydroxy- β -phenylpropionate. Therefore, it appeared that the ester (XL) had not been formed and that the α -hydroxy- β -phenylpropionic ester resulted from the action of the alkaline condensing medium on the bromo-ester. This was in agreement with the work of E. Fischer and Zemlen (10) who prepared inactive α -hydroxy- β -phenylpropionic

acid from the corresponding bromo-acid by heating with water and calcium carbonate, and of McKenzie and Wren (11) who reported the preparation of the active acids from the active bromo-acids by the action of alkali and by water alone.

The main interest centered in the application of this method to the attempted preparation of 2-ketocyclohexylmalonic acid and 2-ketocyclohexylsuccinic acid. When ethyl cyclohexanone-2-carboxylate was condensed with ethyl bromomalonate it was expected that the ester (XLIII) would result, and on hydrolysis, 2-ketocyclohexylmalonic acid (XLIV).



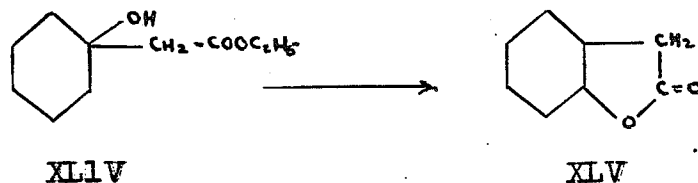
Again it appeared that the reaction did not occur when metallic sodium in benzene was used as the condensing agent, as the original reactants were recovered unchanged, along with an oil, probably ethanetetra-carboxylic ester, as on hydrolysis it produced succinic acid. The ethanetetra-carboxylic ester resulted from the action of two atoms of sodium on two moles of the bromomalonate ester. Ethanetetra-carboxylic ester was made in a somewhat similar manner from sodiomalonate ester and bromine by Kotz and Stalman (12), from chloromalonate ester and sodiomalonate ester by Conrad and Bischoff (13) from 1:2 dibromocyclohexane and ethyl sodiomalonate by Coffey (3), and from bromomalonate ester with sodium iodide in acetone by Finkelstein (14).

When sodium ethylate was used as the condensing agent in place of metallic sodium, monobromoethanetetra-carboxylic ester and ethylenetetra-carboxylic ester were isolated. Conrad and

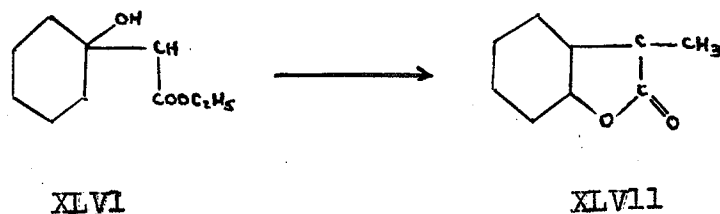
Bruckner (15) reported the preparation of ethylenetetracarboxylic ester by the action of sodium on dibromomalonate in benzene, and Curtis (16) used the action of sodium ethylate on dibromomalonate. The monobromoethanetetracarboxylic ester formed was apparently an intermediate in the formation of the ethylenetetracarboxylic ester. This reaction failed also with ethyl cyclohexanone-2-carboxylate and monobromosuccinic ester. The resulting products were not identified but no 2-ketocyclohexylsuccinic acid was obtained.

METHOD (2)

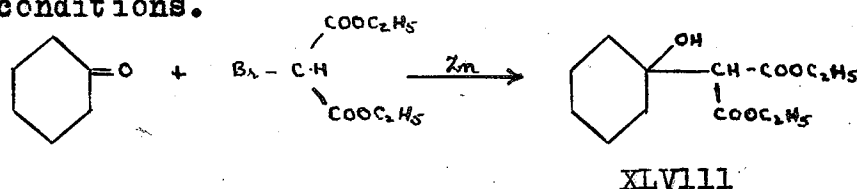
Reformatsky reactions have been utilized in the preparation of α -(1-cyclohexanol) fatty acid esters by Wallach and his associates (17), (18), and by Auwers and Ellinger (20). Boehringer and Sohn (21) prepared the γ -lactones of cyclohexanol fatty acids by boiling these esters with mineral acids. From cyclohexanone, ethyl bromoacetate and zinc, Charlesworth, McRae, and MacFarlane (7) obtained the hydroxy ester (XLIV) and on treatment with mineral acid the γ -lactone of cyclohexanolacetic acid (XLV), identical with that prepared by Coffey (3) and by McRae and co-workers from cyclohexene oxide (1).



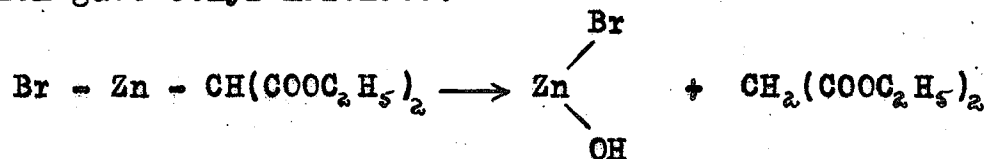
Similarly from cyclohexanone and ethyl α -bromopropionate, they produced the hydroxy ester (XLVI) which with mineral acid gave the γ -lactone of cyclohexanol- α -propionic acid (XLVII).



Although Reformatsky reactions with α -halogenated esters of monocarboxylic acids are fairly common, there appear to be only two recorded cases of the use of α -halogenated esters of dibasic acids in this reaction. In both cases esters of bromomalononic acid were employed. Kohler, Heritage, and Macleod (22) reported that, using unsaturated ketones and methyl bromomalonate, 1:4-addition occurs. Iyer (23) attempted Reformatsky reactions using acetone and ethyl bromomalonate and found that water was eliminated between two molecules of acetone, yielding mesityl oxide, and this was followed by 1:4-addition. In the hope of preparing the hydroxy ester (XLVIII), Charlesworth and co-workers (7) applied the Reformatsky reaction to cyclohexanone and bromomalononic ester under a variety of conditions.



As they found that no reaction occurred, they concluded that a complex similar to a Grignard reagent was formed between the zinc and the bromomalononic ester, and that acidification of this complex gave ethyl malonate.

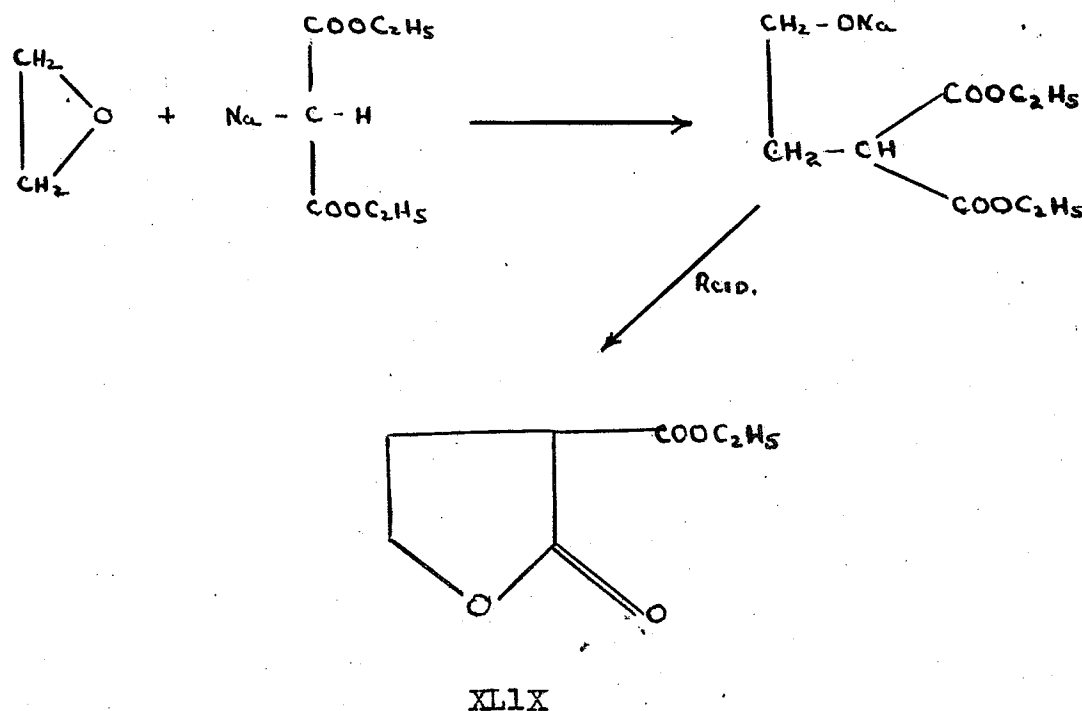


This complex did not react with the cyclohexanone, or only very slightly, as the latter was recovered. In one case, when a large excess of zinc was employed, ethanetetra-carboxylic ethyl ester was obtained, apparently by removal of bromine between two molecules of bromomalononic ester. In similar reactions between ethyl monobromosuccinate and cyclohexanone they isolated nothing but ethyl succinate.

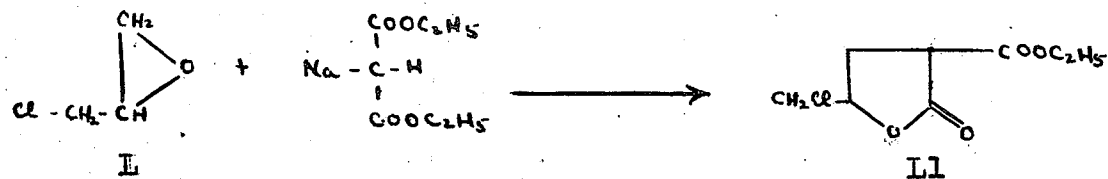
METHOD (3)

Charlesworth, McRae, and MacFarlane (7) made one attempt by this method. 2-Bromocyclohexanone was condensed with the sodio-derivative of the tri-ethyl ester of propane- α, α, γ -tricarboxylic acid. Hydrolysis and heating to decarboxylate failed to yield α -(2-ketocyclohexyl) glutaric acid or any other pure material.

McRae, Charlesworth, Archibald, and Alexander (24) extended the problem by replacing cyclohexene oxide by ethylenic oxides in the previous series of reactions. Prior to that, little work had been done on condensations between sodio-activated methylene groups and ethylenic oxides. Traube and Lehmann (25 & 26) condensed ethylene oxide with ethyl sodio-malonate and on acidification, obtained 2-carbethoxybutyrolactone (XLIX).

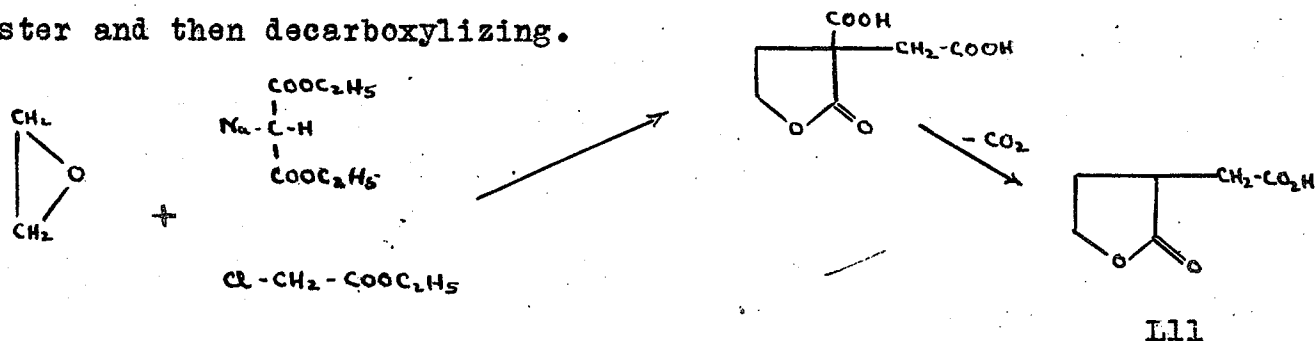


From the epichlorohydrin (L), 4-chloromethyl-2-carbethoxybutyrolactone (LI) was obtained.

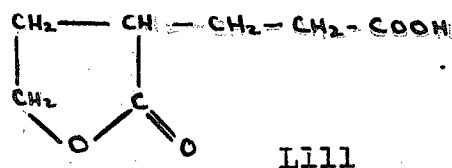


Similar reactions were carried out in which the malonic ester was replaced by acetoacetic ester.

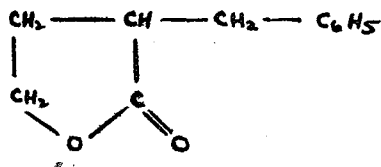
McRae, and colleagues, (24) obtained 2-oxotetrahydrofuran-3-acetic acid (LII) by condensing ethylene oxide, ethyl sodiomalonate and ethyl chloroacetate, hydrolysing the resulting ester and then decarboxylizing.



When ethyl β -bromopropionate replaced ethyl chloroacetate in the above reaction, 2-oxotetrahydrofuran-3-propionic acid (LIII) was obtained.



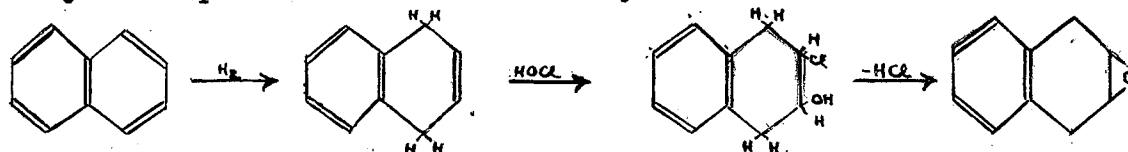
As was true for similar reactions on cyclohexene oxide, it was found that β -halogenated esters could be replaced in condensations of the above type by benzyl chloride, in which case 2-oxo-3-benzyltetrahydrofuran (LIV) resulted.



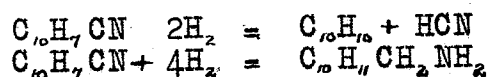
THE CHEMISTRY OF DIHYDRONAPHTHALENE AND DISCUSSION OF RESULTS:

In light of the results obtained by McRae and co-workers, it seems that a logical step in continuing their work would be to replace cyclohexene oxide by tetrahydronaphthalene oxide,

Tetrahydronaphthalene oxide can be synthesized from naphthalene and may be represented schematically as follows:



Bamberger and Lodter (27), while carrying out experiments to determine the effect of sodium and alcohol on aromatic nitriles, found that two classes of substances were formed: Namely the corresponding hydrocarbon; or more generally its dihydro derivative. Thus in the case of naphthonitrile, dihydronaphthalene was obtained



and also an amine

The dihydronaphthalene so formed was a strongly refractive oil boiling at 211°C under a pressure of 113 mm. and solidifying at a low temperature into large glistening tables which melted at 15.5°C .

Dihydronaphthalene was also obtained by the action of sodium and ethyl alcohol on naphthalene. When the dihydronaphthalene so formed was oxidized, it yielded o-phenylenediacetic acid $\text{C}_6\text{H}_4(\text{CH}_2\text{COOH})_2$. Therefore, Bamberger and Lodter concluded that the additional hydrogen atoms in the dihydronaphthalene occupied the para position and not the ortho position.

It is also possible to form 1,4-dihydronaphthalene by direct hydrogenation of naphthalene using platinum or nickel as

a catalyst at 190°C. If hydrogenation is continued, other eight atoms of hydrogen are absorbed to form decalin $C_{10}H_{18}$ (boiling point 190°-191°C at 720 mm.). There is a marked decrease in the velocity of absorption after the first two atoms have been added and tetralin can easily be isolated by interrupting the reaction at the proper stage. Further reduction leads to decalin. This would seem to indicate that 1,4-dihydronaphthalene consists of a benzenoid ring and an aliphatic ring since there is no intermediate stage between tetralin and decalin. It is found, when hydrogenating benzene, that it will only add three moles of hydrogen or none at all.

In connection with his work on lithium naphthalene reactions, the separation of dihydronaphthalene was reported by Schlenk (28). The addition compound of lithium and naphthalene which had been prepared in ethyl ether as solvent, with a reaction time of eight days, was decomposed with alcohol. Both the slowness of this process and the expense of the lithium make this method impractical. Schlenk reported that in experiments of shorter duration, he obtained after alcoholysis an equimolar mixture of naphthalene and dihydronaphthalene.

Scott and Walker (29) carried out experiments with a view to improving the method of preparation of dihydronaphthalene and its homologues with efficient utilization both of the alkali (Na) metal and of the hydrocarbon being reduced. They also hoped to shorten the time required for the reaction. Furthermore, they wished to be able to control the reaction so that dihydronaphthalene or its homologues could be obtained at will, either unpolymerized or polymerized to resinous substances.

Scott and Walker found that dihydronaphthalene and its homologues tend to react with solutions of alkali metal compounds of naphthalene and its homologues to form polymeric alkali compounds which on hydrolysis are converted to resinous polymers. Moreover this reaction between the dihydro compound and the alkali metal compound is profoundly influenced by relatively small temperature changes. At low temperatures this reaction is greatly inhibited; or, if the temperature is sufficiently low, it is completely prevented. Thus the reaction between dihydronaphthalene and disodium naphthalene occurs readily at temperatures of 25°C and higher, but as the temperature is decreased below 25°C , the reaction is progressively inhibited and at temperatures around -30°C the reaction is not appreciable within a reasonable length of time.

One possible reason for the low yield of dihydronaphthalene obtained by prior methods is based on the fact that ordinarily not more than one gram atom of alkali metal will react with one gram molecule of naphthalene in reasonable time: e.g. several hours. This proportion of reacted metal is equivalent to the formation of one mole of dimetal naphthalene, leaving one mole of naphthalene unreacted. When the reaction mixture is hydrolysed, the resulting hydrolysis product theoretically is an equimolar mixture of naphthalene and dihydronaphthalene. Scott and Walker claim that by their method they were able to convert 90% or more of the naphthalene to dihydronaphthalene in a single operation. The product can be analysed by titrating with solutions of bromine in chloroform at 0°C . Each molecule of dihydronaphthalene absorbs one molecule of bromine without liberation of HBr .

Scott and Walker allowed the hydrocarbons to react with sodium in a solvent medium comprising substantial amounts of certain ethers. The ethers used for this purpose were relatively inert to sodium and to the sodium hydrocarbon compound which was formed in the reaction. They may be divided into two classes as follows:-

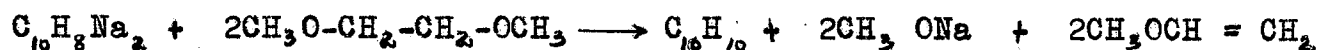
1. Dialkyl mono-ethers having a methoxy group and in which the atomic ratio of oxygen to carbon is not less than 1:4. Examples of this group are dimethyl ether and methyl ethyl ether.
2. Poly-ethers - that is, ethers having more than one ether oxygen linkage; for example, the fully alkylated derivatives of ethylene glycol or glycerol.

If methyl ether is used as a solvent medium, the previously known sodium reactions take place many times faster than in ethyl ether. With this solvent, it is possible to increase the scope of the reaction to include naphthalene and diphenyl as well as other hydrocarbons. If ethyl ether is added to a mixture then the reaction is reversed and the original hydrocarbon and elementary sodium are obtained. With a concentrated solution of hydrocarbon in pure methyl ether, it is possible to dissolve one or two gram atoms per litre in two hours. Methyl ethyl ether is the only other mono-ether in which these reactions can readily occur. The formation of sodium naphthalene is slow but detectable in methyl propylether.

Scott, Walker and Hansley (29) in seeking suitable solvents that are liquid at room temperature discovered that the

dimethyl ether of ethylene glycol (boiling point 85°C) is a substance equivalent to dimethyl ether as a solvent for sodium reactions. Contrary to conclusions that might have been drawn from the behavior of the mono-ethers, it was found that all fully alkylated glycols and polyhydric alcohols are effective solvents for sodium addition reactions. It was also found that trimethylamine and a few other amino compounds are effective although they offer little advantage over the ethers.

For most purposes dimethyl ether and the dimethyl ether of ethylene glycol are the most suitable solvents for the reaction and the latter is more convenient by reason of its boiling point. It is, however, slowly attacked by sodium naphthalene at room temperature with the formation of methyl vinyl ether presumably in accordance with the equation



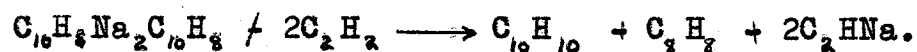
This methyl vinyl ether was identified by its boiling point and unsaturation towards bromine.

The preparation of the special solution is required not merely for the initiation of the reactions but for the existence of the sodium naphthalenes. This can be shown by preparing a solution of sodium naphthalene in dimethyl ether and then evaporating at room temperature. The dark green solution deposits a very dark green solid which changes colour with the loss of the last traces of ether. The solid will, on treatment with water, evolve nearly the theoretical amount of hydrogen as such. When sodium naphthalene is treated with water no hydrogen is evolved. Thus for most purposes the isolation of sodium naphthalene in the solid state is not attempted since its reactions are con-

veniently carried out in solution.

The reactions of sodium naphthalene can be divided into two classes. In the first sodium is recovered unchanged, the solution behaving much like dissolved sodium. In this class may be mentioned reactions with mercury, oxygen and benzyl chloride.

In the second class of reactions, the naphthalene is reduced to dihydronaphthalene or its derivatives depending upon the reagent used. With water, alcohol and a wide range of organic compounds capable of forming sodium derivatives, where the sodium replaces hydrogen, the products are dihydronaphthalene and the sodium compound of the material used as a source of hydrogen. e.g. with acetylene



In general, the only requirements for the formation of sodium naphthalene and related compounds in dimethyl ether and other active solvents are that the solvent be pure and dry and that the hydrocarbon be reasonably pure. It is also imperative that a clean surface of the alkaline material be exposed in order to initiate the reaction. Once started the reaction thoroughly cleans any metal surface that was not originally clean. Impurities such as H_2O , methanol and CO_2 prevent the reaction from starting by forming products which coat the surface of the alkali metal as soon as it is exposed. If they are only present in traces, however, persistent scratching of the surface will eventually lead to their destruction and the reaction will proceed.

In the present project, it was decided to attempt the preparation of dihydronaphthalene by the method of Scott, Walker and Hansley, using the dimethyl ether of ethylene glycol as the

solvent. The dimethyl ether of ethylene glycol was not available commercially and had to be synthesized. The method of Clarke (30) was investigated, in which the sodium salt of methyl cellosolve was treated with methyl sulphate. The best yield obtained on several runs was 23% based on the methyl cellosolve. Furthermore, the residue left after distilling off the dimethyl ether of ethylene glycol was a black resin from which none of the methyl cellosolve could be recovered.

Attention was then turned to the method of Capinjala (31) in which the methylation of methyl cellosolve was carried out by the use of methyl chloride. The yield based on sodium was 78%. While the yield based on sodium was high, that based on the methyl cellosolve was only 19.5%. However, this method had the advantage over that of Clarke in that the unreacted methyl cellosolve was recoverable by distillation.

The dihydronaphthalene prepared by the method of Scott and Walker was a white solid similar in appearance to naphthalene and melted at 27°C.

Bamberger and Lodter prepared the chlorohydrin of dihydronaphthalene (27) by treating dihydronaphthalene with hypochlorous acid. A convenient source of this acid was obtained by the acidification of monochlorourea solution with glacial acetic acid which according to Detoeuf (33) does not favour the production of secondary dichloro products and also hastens the reaction by acting as a solvent. A 10% excess of dihydronaphthalene was used in order to eliminate, as far as possible, the formation of dichloro products. By this method, hypochlorous acid solutions in strengths of about 14% were obtained.

Dihydronaphthalene was found to be insoluble in monochlorourea solution. Furthermore, there was no evidence of reaction after continued stirring. Gentle heating did not lead to a reaction. It was concluded that probably the lack of intimate contact between the dihydronaphthalene and the monochlorourea solution was responsible for the failure to react. Hence a slight amount of the dimethyl ether of ethylene glycol was added in order to overcome this but still no chlorhydrin was obtained.

The dihydronaphthalene prepared by Bamberger and Lodter (27) was a yellow oil boiling at 210°C at 760 mm. Six runs were made using this method and the total product treated with monochlorourea solution but no reaction occurred, the dihydronaphthalene being recovered by separation and distillation. Thus it appeared that the failure to react must have been due to monochlorourea inhibiting the reaction rather than to the lack of intimate contact between the reagents since Bamberger and Lodter prepared the chlorhydrin from reagents which did not have any more intimate contact.

Thus the monochlorourea method was abandoned and an attempt made to prepare the chlorhydrin by the method employed by Bamberger and Lodter in which the hypochlorous acid solution was obtained by the action of boric acid on a solution of bleaching powder which had previously been treated with calcium carbonate. The authors state that the formation of the chlorhydrin should have progressed considerably within fifteen minutes as shown by the consistency in the flask. However, repetitions of their procedure did not show this. The reaction mixtures were allowed to shake over night. After that period, an oily mass containing crystals lay at

the foot of the flask. The crystals were separated off by suction, washed with water and hot ligroin. The crystals were identified as calcium borate which had separated out and had carried down the unchanged dihydronaphthalene. Runs were made using acetic acid in place of boric acid in order to overcome the effect of the delayed crystallisation of calcium borate, and hypochlorous acid solutions were prepared from bleaching agents in order to obtain more concentrated solutions of the acid. However, these modifications were unsuccessful.

Leroux (34), in his study of the hydronaphthalene series, prepared dihydronaphthalene by the method of Bamberger and Lodter. He purified the product by freezing it and allowing it to partially melt, and poured off the liquid portion. By repeating this procedure several times, he was able to separate the low melting dihydronaphthalene from the unreacted naphthalene. He also prepared the iodohydrin of dihydronaphthalene by reacting dihydronaphthalene with yellow mercuric oxide and iodine.

A study of the iodohydrins of cyclohexene, amylene and dihydronaphthalene was undertaken. If the yields of these iodohydrins were high enough they would give a means of arriving at the respective oxides by removal of hydrogen iodide from the iodohydrin by treatment with sodium hydroxide solution.

The iodohydrins were obtained but they did not crystallise out. The oils were distilled at low temperatures but there was a marked tendency for the iodohydrin to break down.

The failure of the iodohydrins to crystallise out and, therefore, the inability to purify them eliminated their use as a means of arriving at the oxides. It was resolved to carry out a thorough study of the methods available for the preparation of chlorohydrins. It was found that four main procedures are

available:-

1. The direct action of chlorine and water.
2. The action of Cl_2 or CaOCl_2 with CO_2 or CaCO_3 .
3. The use of Cl_2 in the presence of Mercuric oxide and water.
4. Detoeuf's urea method (33).

The first method is particularly adapted to gaseous reactions though it can also be used for liquids by a modification of the apparatus.

For liquids, the chlorine is usually dissolved in water and the hypochlorous acid solution added to a suspension or emulsion of the olefin in water, with vigorous stirring (36).

The second method, employing calcium compounds, was the one used by Bamberger and Lodter in their preparation of the chlorohydrin of dihydronaphthalene. Wohl and Schweitzer (37) prepared hypochlorous acid solution in a similar way by passing chlorine gas through a solution of sodium carbonate. A trial run was made by this method and titration showed 2.21% hypochlorous acid to be present.

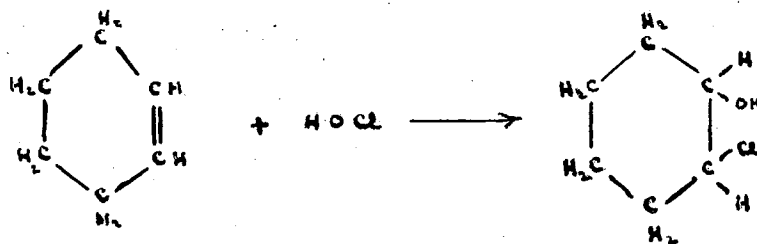
Pedro Sanchez (37) described a method in which an aqueous solution of lime and an acid were combined in sufficient quantity to produce a precipitate not substantially soluble in aqueous solution. While the precipitate was in suspension, chlorine gas was injected into the solution until the required quantity of Cl_2 had been absorbed, after which the precipitate was allowed to settle and the clear chlorinated liquid was filtered or drawn off, containing stable hypochlorous acid in solution.

The third main method employing mercuric oxide is an older procedure and is briefly described by Fortey (38). It consists of passing chlorine into a freshly prepared suspension of mercuric oxide



Coleman and Johnstone (39) described the details of this procedure as follows:-

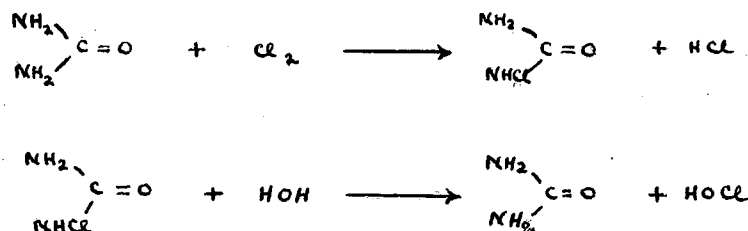
A solution of mercuric oxide (25 grams) in water (500 cc) was placed in a five litre flask and cracked ice (800 grams) was added, and then a rapid stream of chlorine passed into the mixture which had to be kept below 5°C . The addition of the chlorine was continued until the yellow precipitate of mercuric oxide just disappeared. Cold nitric acid (600 cc of 1.5 N) were slowly added with stirring. Coleman and Johnstone used this solution in the preparation of cyclohexene chlorohydrin.



A similar method was outlined by Ourisson and Kastner (40) in which a suspension of mercuric oxide in carbon tetrachloride was treated with chlorine to give Cl_2O in solution in carbon tetrachloride. When this latter solution was treated with water, a solution of mercury-free hypochlorous acid was obtained. By this process it was possible to form very concentrated solutions of hypochlorous acid, which were practically free of chlorides and free chlorine. They were also remarkably stable.

A circulating method based on this reaction has been patented in which only a small amount of chlorine was reacted at once. The Cl_2O was extracted with water in such small amounts as not to absorb much free chlorine. The suspension of mercuric oxide in carbontetrachloride was then chlorinated once more.

Dateouf's method using monochlorourea has already been mentioned. The mechanism of this reaction is the hydrolysis of the monochlorourea with the consequent formation of hypochlorous acid. This acid reacts with the olefin in solution to give the chlorohydrin which is extracted from the mixture by ether.



The acetic acid added to the monochlorourea olefin mixture makes the reaction go more rapidly but must not be too strong, otherwise chlorine is liberated.

The mechanism of addition of the hypochlorous acid to an olefin generally follows Markownikov's rule: i.e.

1. When the carbon atoms of the double bond are unequally substituted, the hydroxyl group goes to the most substituted atom.
2. When the carbon atoms are equally substituted, the hydroxyl group goes to the carbon farthest from the end of the chain.

When the general methods available for the preparation of hypochlorous acid are considered with regard to the present

problem, it is obvious that the one involving the direct action of chlorine and water is the least applicable. The one involving the action of Cl_2 or CaOCl_2 with CO_2 or CaCO_3 has been tried, namely in the method of Bamberger and Lodter. Detoef's method did not prove successful. The procedure of producing hypochlorous acid solutions by treating a suspension of mercuric oxide in carbon tetrachloride sounded most promising in that concentrated solutions of the acid could be produced. It was felt, however, that a more direct route could be taken to arrive at concentrated solutions of hypochlorous acid; namely, through the acidification of saturated solutions of calcium hypochlorite. Solutions produced in this manner were used in attempts to produce the chlorohydrins of cyclohexene, amylene and dihydronaphthalene. The acidification of the calcium hypochlorite solution was carried out in two ways in each case. One method used acetic acid as the acidifying agent while the other used boric acid. It was found that acetic acid gave better results. Yields of the chlorohydrin of cyclohexene were comparable with those obtained by other methods. In the case of amylene chlorohydrin, they were lower.

On placing dihydronaphthalene in a saturated solution of calcium hypochlorite and then slowly adding acetic acid, a considerable amount of heat was evolved and the reaction mixture was placed in a salt-ice mixture. No attempt was made to isolate the chlorohydrin but rather to convert it to the oxide by the method of Bamberger and Lodter (41). After distilling off the alcohol used as a solvent, it was found that a liquid began to distil over at 60°C . This colorless liquid continued to distil over and the temperature rose gradually but steadily to 205°C .

In the range 205°C - 217°C , the oil crystallized as it passed from the condenser. The temperature climbed slowly but steadily to 259°C (739 mm.) as the last traces of oil passed over. However, the oil coming over above 217°C showed no signs of crystallizing.

Bamberger and Lodter (41) reported that tetrahydronaphthalene oxide melted at 43.5°C . It distilled at 257°C - 259°C (715 mm.) to a colorless oil which quickly set to splendid silvery-white, naphthalene-like plates. It was very volatile and distilled not only with steam but also of its own accord. Even at 40°C - 50°C , it distilled over as an oil which quickly set to long needles. It was slightly soluble in ether, alcohol, benzene, chloroform, boiling ligroin, very slightly soluble in cold ligroin and significantly soluble in water, especially warm water. From solutions of lye and sodium chloride, it precipitated as iridescent leaflets, and from water as naphthalene-like plates.

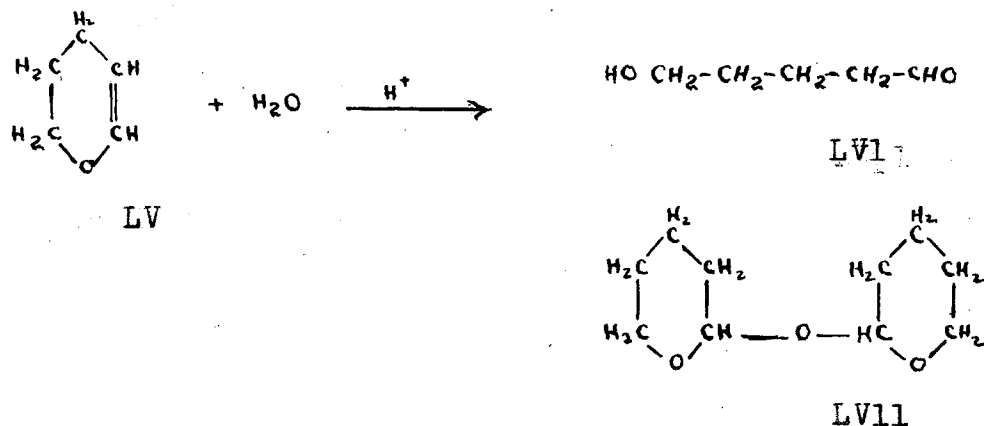
Thus the only similarities between the product obtained using Matheson's H.T.H. and tetrahydronaphthalene oxide are their volatility at low temperature and the temperature at which the oil finally distills. On the other hand, they differ in so far as the product of the H.T.H. method shows no signs of needle-like crystals in the low boiling range nor does the material distilling over at 257°C .

Bamberger and Lodter (46) stated that when tetrahydronaphthalene chlorohydrin was treated with alkalies, three isomerides of the formula $\text{C}_{10}\text{H}_{16}\text{O}$, a dihydric alcohol, $\text{C}_{10}\text{H}_{14}\text{O}_2$,

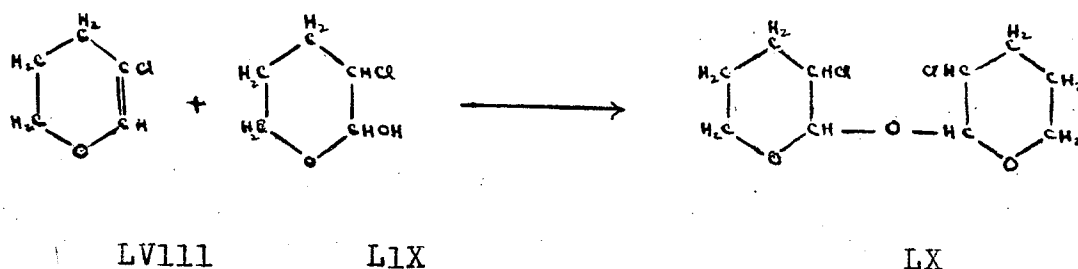
and naphthalene were formed depending on the conditions of the experiment.

Difficulty has been experienced in the preparation of chlorohydrins similar in structure to that of tetrahydronaphthalene chlorohydrin. Charlesworth and his co-workers attempted the preparation of acenaphthylene chlorohydrin without success. Recent research carried out on dihydropyran may offer an explanation for lack of chlorohydrin formation.

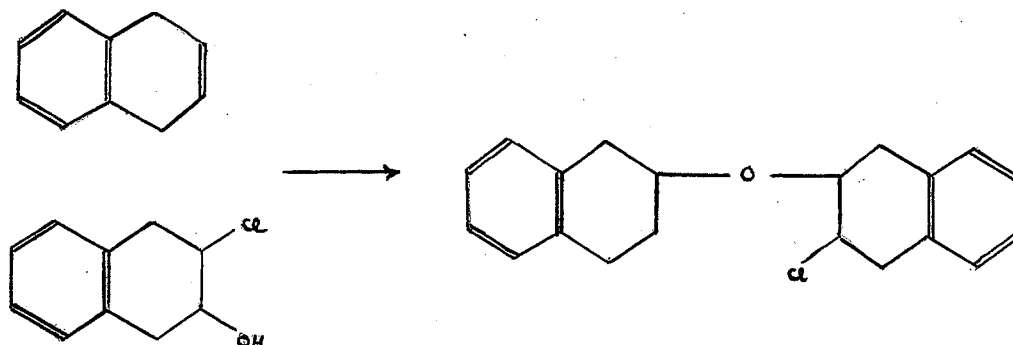
Dihydropyran (LV) adds one mole of water to the double bond when hydrolysed with dilute acid solutions. This is followed by opening of the ring to form Δ -hydroxyvaleraldehyde (LVI) plus a bicyclic acetal, di-2-tetrahydropyryl ether (LVII) as a by-product.



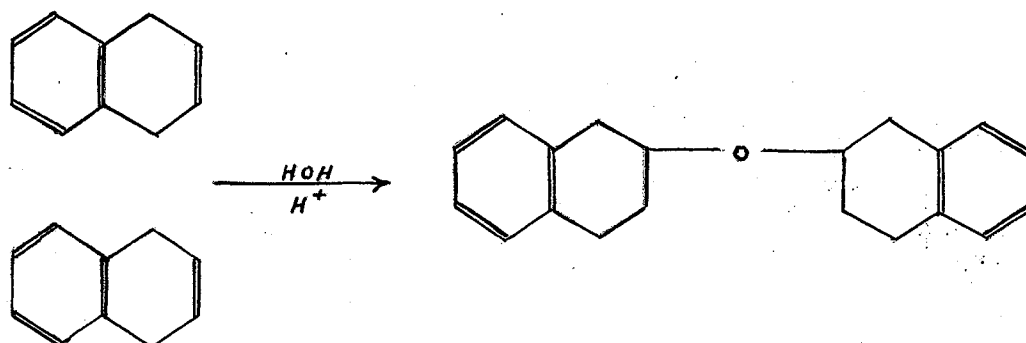
British research workers (47) have found that 3-chlorodihydropyran (LVIII) and 2-hydroxy-3-chlorotetrahydropyran (LIX) react to form bis-(3-chloro-2-tetrahydropyryl)ether, (LX).



Thus in attempts to form tetrahydronaphthalene chlorohydrin, the latter may react immediately on formation with the unreacted dihydronaphthalene.



It would seem that ether formation of this type might be reduced by carrying out the reaction in dilute solution. However, under these conditions, hydrolysis of the dihydronaphthalene might occur, thus resulting again in ether formation.



The dimethyl ether of ethylene glycol, in which dihydronaphthalene and hypochlorous acid are mutually soluble, might be used as a diluent, thus reducing hydrolysis of the dihydronaphthalene to a minimum.

The conversion of tetrahydronaphthalene chlorohydrin to tetrahydronaphthalene oxide would seem to require the neutralization at high dilution in order to prevent ether formation, as the removal of hydrochloric acid might occur between two molecules of the chlorohydrin in place of one.

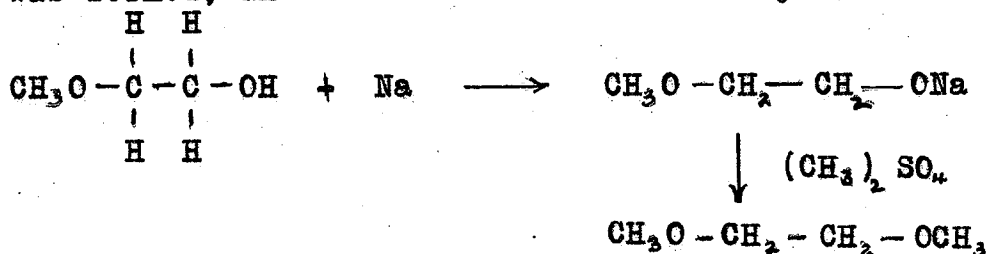
EXPERIMENTAL

PREPARATION OF DIMETHYL ETHER OF ETHYLENE GLYCOL

Method of Clark, H.T. (30)

The disodium derivative of ethylene glycol was prepared according to the directions of Lippert (43) from 21 grams of glycol and 15 grams of sodium in ethyl alcohol, and mixed with 82 grams (2 moles) of methyl sulphate. The mixture was heated in a distilling flask on an oil bath. At 90°C a violent reaction set in; a liquid distilled over; and a large quantity of black residue remained in the flask. The distillate was boiled with solid potassium hydroxide, and the clear liquid separated and distilled. The fraction boiling up to 90°C was repeatedly boiled with metallic sodium till no further reaction took place, filtered and distilled over sodium. The pure substance was obtained as a colorless liquid boiling at 78°C (750 mm), miscible with water and possessing a sharp ethereal odor. The yield was poor. Lippert who prepared this ether by heating the disodium salt of ethylene glycol with methyl iodide for over a week, states that it boils at 82° - 83°C (713 mm) but it is questionable whether his product was pure, as his determination of its vapour density was distinctly too low. This ether yields no precipitate with aqueous mercuric chloride and does not react with bromine at 0°C or 20°C.

Clark's method was carried out using cellosolve (CH₃) as the starting material in place of ethylene glycol. The sodium salt was formed, and then reacted with dimethyl sulfate.



As the reaction was strongly exothermic on the addition of the methyl sulfate, a condenser was attached by a side arm from the reaction flask. The methyl sulfate was added through a dropping funnel. Thus any dimethyl ether of ethylene glycol which formed and commenced to distill off due to the heat of the reaction was recovered. Despite this, the yields obtained were poor. Several runs were made. The best result was obtained on a trial using 65 grams of cellosolve (methyl) and 15 grams of sodium, from which 21.3 gms. of the dimethyl ether of ethylene glycol were formed, representing a yield of 23.7%.

PREPARATION OF THE DIMETHYL ETHER OF ETHYLENE GLYCOL

Method of Capinjola (31)

The methyl cellosolve (1,830 grams) was placed in a three-litre, three-necked flask equipped with a reflux condenser and mechanical stirrer. Sodium (138 grams) was added portionwise in small pieces. As the sodium dissolved, the mixture thickened and became dark brown in colour. When all the sodium had dissolved, the flask was fitted with a thermometer and an inlet tube extending below the surface of the solution. Methyl chloride was then passed into the solution at such a rate that very little escaped the reaction. The reaction started immediately and proceeded smoothly and rapidly. Some heat was evolved and this was removed by means of a water bath applied when the temperature of the mixture reached 60°C. When the reaction was complete, as determined by the gain in weight, the mixture was cooled and the liquid portion was decanted from the sodium chloride. The time for complete methylation was about three hours. The liquid portion was distilled from an ordinary distilling flask, collecting the material distilling

below 123°C. Fractional distillation of this material gave 422 grams of dimethyl ether of ethylene glycol boiling at 83.5°C - 84.0°C. The yield based on sodium was 78%.

Capinjola's method was modified slightly in order to obtain a greater conversion of the methyl cellosolve to dimethyl ether of ethylene glycol. The sodium was added in stages. In the first step, sodium was added till the solution began to thicken. It was found that this occurred when the mole ratio of sodium to methyl cellosolve was one to four. Methyl chloride was then bubbled through the solution till the gain in weight of the mixture showed that the greater part of the sodium salt had been converted to dimethyl ether of ethylene glycol. Then addition of methyl chloride was halted and another mole of sodium was dissolved in the solution. Once more methyl chloride was bubbled through the mixture. Finally the mixture was fractionally distilled and the unconverted methyl cellosolve was recovered.

Trial I

Wt. Methyl Cellosolve	304	gms.
Wt. Sodium	22	gms.
Wt. Dimethyl Ether of Ethylene Glycol....	52.5	gms.
% Yield(based on Methyl Cellosolve).	14.6	%.

Trial II

Wt. Methyl Cellosolve	304	gms.
Wt. Sodium	22	gms.
Wt. Dimethyl Ether of Ethylene Glycol....	50.5	gms.
% Yield(based on Methyl Cellosolve).	14.0	%

Trial III - Intermittent addition of Sodium.

Wt. Methyl Cellosolve 152 grms.

Wt. Dimethyl Ether of Ethylene Glycol.... 52 gms.

% Yield(based on Methyl Cellosolve). 28.0 %

PREPARATION OF SODIUM NAPHTHALENE SOLUTION

Method of Scott, Walker, and Hansley. (29)

A molal solution (1 litre) of naphthalene in pure dry dimethyl glycol ether was placed in a two-litre, three-necked flask equipped with a mercury sealed stirrer in which an atmosphere of pure dry nitrogen was maintained. Sodium (25 grams) was then added, the metal being cut in the form of sticks 2 to 3 cms. long and 3 to cms. square on the ends. After the sodium had been added, the mixture was agitated mechanically. The stirring was rapid at first but was decreased considerably after the reaction had commenced. The reaction mixture was kept between -10°C and -30°C in order to prevent polymerization of the 1,4-dihydronaphthalene formed. At 20°C to 25°C the reaction was completed in about two hours. The unreacted sodium was stuck together in a single piece and was removed from the mixture by a forceps.

The progress of the reaction was determined from time to time by the removal of a small sample of the reaction mixture and determining its sodium content, after dilution with alcohol, by titration with standard acid using methyl red. This did not discriminate between sodium naphthalene and other suspended or dissolved sodium compounds in solution, but when pure, it gave a close approximation to the sodium naphthalene that had been formed.

PREPARATION OF SODIUM NAPHTHALENE SOLUTION AND

1,4-DIHYDRONAPHTHALENE

Scott and Walker's Modified Method. (29)

A molal solution (1 litre) of naphthalene in pure dry dimethyl glycol ether was placed in a two-litre, three-necked flask equipped with a mercury sealed stirrer in which an atmosphere of pure dry nitrogen was maintained. Approximately 2 gram atoms of sodium per gram molecule of naphthalene in solution were placed in a perforated container which was suspended in the solution. Stirring was commenced and the reaction carried out at room temperature under the atmosphere of nitrogen. As soon as the reaction between the sodium and the naphthalene had commenced as indicated by the formation of a green colour around the sodium, the hydrolysing agent, water, was slowly added to the solution, either continuously or intermittently. As the reaction proceeded, care was taken that the rate of addition of the water was sufficient to prevent the spread of the green colour throughout the solution but not great enough to prevent the formation of the green colour on the surface of the sodium or in close proximity thereto. It was found preferable to add the water in such a manner that the sodium particles were covered with a film of the green sodium naphthalene compound but the reaction mixture was substantially free from the green compound. If the water was added too rapidly, it would react with the sodium, which would be indicated by the formation of a white coating of sodium oxide on the sodium particles. The sodium hydroxide formed by the hydrolysis being insoluble in the solvent ether, formed a precipitate. When the reaction was complete, the hydrolysed solution was saturated with carbon dioxide prior to filtration to convert the sodium

hydroxide to sodium bicarbonate which was easier to filter out than the sodium hydroxide. The filtrate was then distilled at atmospheric pressure, the dihydronaphthalene distilling over at 205°C to 210°C. Repeated trials were made using this method. In each case the dihydronaphthalene was obtained as a white crystalline solid, whereas the method of Bamberger and Lodter (27) yielded a yellow oil. The yield varied from 80 - 85% but the product was contaminated with naphthalene. As the boiling point of naphthalene is 217°C an efficient fractionation column would be required to carry out the separation. However, the impurity presented no problem in this case as it was unreactive to hypochlorous acid and could be more readily removed once tetrahydronaphthalene oxide had been formed.

PREPARATION OF 1,4-DIHYDRONAPHTHALENE

Method of Bamberger and Lodter (27)

A boiling solution of naphthalene (15 grams) in absolute alcohol (300 cc.) was slowly run onto sliced sodium (22.5 grams) in a round bottomed, two-litre flask, and the solution boiled till the metal dissolved. Part of the alcohol was recovered by distillation through a fractionating column and the dihydronaphthalene driven over by a current of steam, and then taken up from the distillate by ether. The dihydronaphthalene was obtained as a yellow oil boiling at 210°C. The yield obtained by this method was 78% crude product.

It was found that about 50% of the alcohol was recoverable. The crude product contained from 15 to 25% impurity which was chiefly unchanged naphthalene. A larger portion of sodium tended to convert the dihydronaphthalene formed to

tetrahydronaphthalene. Thus the yield obtainable on a run of the above proportions was about 10 grams of pure product.

In order to make this method useful in preparing larger quantities of dihydronaphthalene, a greater recovery of the absolute alcohol was necessary. Therefore, six runs were made in which the boiling solution of naphthalene in absolute alcohol was treated with sodium. The resulting solutions were then poured into a three-litre, round bottomed flask. The greater part of the alcohol was distilled through a fractionating column. Then heating was continued over an air bath, taking care not to char the solid material. It was found that by this procedure, the greater part of the absolute alcohol was recoverable.

PURIFICATION OF 1,4-DIHYDRONAPHTHALENE

Method of Strauss and Lemmel (44)

The crude 1,4-dihydronaphthalene was shaken in an ethereal solution with an aqueous solution of mercuric acetate. A white crystalline mercury compound was formed. This compound was washed with ether and then dissolved in benzene, when a slight residue was obtained. This was the mercury compound of the isomeric 1,2-dihydronaphthalene present in the starting material. The pure mercury compound melted from 119° - 120°C and was obtained by evaporating off the benzene. When the mercury compound was treated with a 30% solution of hydrochloric acid, 1,4-dihydronaphthalene leaflets were obtained, melting at 24.5° - 25°C and boiling at 94.5°C at 17 mm. pressure.

PREPARATION OF MONOCHLOROUREA SOLUTION

Method Detoef (33)

A mixture of urea (480 grams), precipitated chalk (240 grams), and water (240 cc.) was placed in a three-litre flask equipped with an inlet tube projecting under the surface of the mixture for the introduction of the chlorine and an outlet tube to the hood for the escape of the carbon dioxide. The flask was cooled in ice. Chlorine gas from a cylinder was passed in until the weight increased from 250 to 280 grams. The flask was agitated from time to time. The chlorine was absorbed fairly rapidly at first, but more slowly towards the end. The chlorination took from 4 to 5 hours. The solution was then diluted to 1400 cc. and the excess chalk filtered off and washed with an additional 100 cc. of water. The strength of the solution was determined by withdrawing a 1 cc. sample, diluting with 25 cc. of water, adding 10 cc. of 1.8 M. potassium iodide solution, acidifying with glacial acetic acid and titrating with standard thiosulphate solution, using starch as an indicator.

A solution of monochlorourea was prepared according to the above procedure, using one third of the stated quantities. After bubbling chlorine slowly through the reaction mixture for six hours, the increase in weight was found to be 77 grams. After filtration, the solution was titrated with standardized sodium thiosulfate, and the following results were obtained:-

1 ml. HOCl Solution = 41.4 ml. Sodium Thiosulfate Solution.

But 1 ml. Sodium Thiosulfate = .003509 gms. HOCl.

1 ml. HOCl Solution contained .14527 gms. HOCl.

% HOCl in the Solution = 14.53%.

After three days, the solution was titrated again in order to determine its stability:-

1 ml. HOCl Solution = 40.5 ml. Sodium Thiosulfate Solution.

But 1 ml. Sodium Thiosulfate = .003509 gms. HOCl.

% HOCl in the Solution = 14.21%.

ATTEMPTED PREPARATION OF TETRAHYDRONAPHTHALENE CHLOROHYDRIN
USING DETOEUF'S SOLUTION

In order to prevent the formation of the dichloride, a 10% excess of dihydronaphthalene was employed in the reaction. When the dihydronaphthalene (16 grams) was added to the hypochlorous acid solution (35.8 ml.) no reaction occurred. Slight heat was applied in an attempt to induce the reaction to take place. The dihydronaphthalene melted and a red oil separated to the bottom of the flask when stirring ceased. The oil was separated off, washed with water, and then dried over anhydrous calcium chloride. On distillation, the oil proved to be unreacted dihydronaphthalene.



PREPARATION OF TETRAHYDRONAPHTHALENE CHLOROHYDRIN

Method of Bamberger and Lodter (27)

Bleaching powder (400 grams) was shaken with water (2 litres) at 40°C and then treated with calcium carbonate (300 grams) and left to stand for one day (in darkness). The calcium carbonate was then filtered off on a Buchner Funnel and 300 grams of pulverized boric added, which by shaking was soon almost completely in solution. Once more the solution had to be filtered, following which an abundant quantity of crystalline borate settled at the bottom. To the clear solution, dihydronaphthalene (25 grams) was now added. Within fifteen minutes the formation of chlorohydrin had progressed considerably, as was apparent by the consistency in the flask. After standing in the dark for twenty-four hours with occasional shaking, the greater part was converted to a crystalline mass, which was filtered strongly on a suction pump and eventually washed with water and then thoroughly with low boiling ligroin. It was then, especially if it had been dried on a porcelain plate and was oil free, found to melt at 105°C - 115°C and represented after recrystallising from alcohol almost pure chlorohydrin. From 120 grams of dihydronaphthalene were obtained on the average not more than 95 - 100 grams of raw product. This represented a yield of from 53.5 to 59.5%.

Following Bamberger's method, a hypochlorous acid solution containing 1.75% hypochlorous acid was obtained. The dihydronaphthalene (16 grams) was added to the hypochlorous acid solution (300 ml.) with constant shaking. There was no

evidence of a reaction taking place after fifteen minutes. The mixture was left on the mechanical shaker over night. At the end of that time, oil saturated crystals lay at the bottom of the flask. The crystalline material was filtered on a suction pump and washed with ligroin. The solid was found to be sodium borate which had crystallized out of the solution.

This procedure was repeated four times. The ligroin washings were combined and evaporated, yielding a brownish solid. This was recrystallized from alcohol and found to have a melting point of 113°C . Bamberger reported the melting point of tetrahydronaphthalene chlorohydrin as 114°C . A total 1.5 grams of tetrahydronaphthalene chlorohydrin was obtained from the four trials.

ATTEMPT TO FORM THE CHLOROHYDRIN BY USE OF BLEACHING SOLUTION (JAVEX)

Bleaching solution (Javex - 200 grams) was treated with boric acid (100 grams). The crystalline borate crystallized out. After standing twenty minutes, the solution was filtered by suction. The solution was then titrated with standard sodium thiosulphate and found to contain 2.63% hypochlorous acid. Dihydronaphthalene (17 grams) was added to the acid solution, an excess of dihydronaphthalene being used to prevent the formation of the dichloride of dihydronaphthalene. A slight amount of heat was liberated on shaking. At the end of an hour, the oil had become more viscous. Titration with standard sodium thiosulphate showed the presence of

hypochlorous acid and therefore, the solution was allowed to stand over night. The oil was extracted with ether and dried over anhydrous calcium chloride. The excess ether was distilled off. The oil was found to distill over between 205°C and 210°C and was therefore unreacted dihydronaphthalene.

ATTEMPT TO FORM THE DIHYDRONAPHTHALENE CHLOROHYDRIN BY
THE USE OF BLEACHING SOLUTION (JAVEX)

Second Method:

The rated available chlorine content of the commercial solution was given in terms of sodium hypochlorite (12%). The boric acid treatment of this solution gave only weak acid solutions. It was decided to form the hypochlorous acid by the addition of glacial acetic acid to the solution. Assuming the available chlorine to be 12% present as sodium hypochlorite:-

100 grams of bleaching solution contained 12 grams Cl_2 .

35.5 grams of chlorine are present in 52 grams of HOCl .

100 grams of solution contain $\frac{12}{35.5} \times 52 = 17.5$ gms. HOCl .

Theoretically, 62 grams of HOCl combine with 130 grams of dihydronaphthalene. Therefore, theoretically, 17.5 grams of HOCl combine with $\frac{17.5}{62} \times 130 = 36.7$ grams of dihydronaphthalene.

A 10% excess of dihydronaphthalene was used to prevent dichloride formation.

Thus a total of 40.3 grams of dihydronaphthalene was added. The reaction warmed up on the addition of the acetic acid to the mixture of the bleaching solution and dihydronaph-

thalene. The solution was left shaking over night in darkness. The solution was extracted with ether and treated with sodium carbonate to remove any acetic acid present. The solution was then washed and dried over anhydrous calcium chloride. The ether was distilled off leaving an oil which proved to be dihydronaphthalene.

PREPARATION OF HYPOCHLOROUS ACID SOLUTION

Method of Wohl and Schweitzer (45)

Sodium bicarbonate (50 grams) was dissolved in water (600 ml.). The solution was cooled in an ice bath. Bright light was excluded and a vigorous stream of chlorine bubbled through the solution until the bicarbonate had just disappeared. This point was readily recognized from the fact that a sample portion on warming with barium chloride solution gave no precipitate.

A hypochlorous acid solution (1200 ml.) was prepared according to this method. Titration with standardized sodium thiosulphate gave the following results:-

1 ml. HOCl Solution = 6.3 ml. Sodium Thiosulfate Solution

But 1 ml. Sodium Thiosulfate Solution = .003509 gms. HOCl.

1 ml. HOCl Solution contained .02211 grams HOCl.

% HOCl in the Solution = 2.21%

ATTEMPTED PREPARATION OF TETRAHYDRONAPHTHALENE CHLOROHYDRIN
USING WOHL AND SCHWEITZER'S SOLUTION

Dihydronaphthalene (16 grams) was added to the hypochlorous acid solution (250 ml.). The mixture was shaken over night. There was no appearance of crystals. The oil at the bottom of the flask was separated from the solution and dried over anhydrous calcium chloride. On distillation the oil proved to be unreacted dihydronaphthalene.

PREPARATION OF THE IODOHYDRIN OF CYCLOHEXENE

Method of Brunel (35)

Cyclohexene (40 grams) was dissolved in ether, free of alcohol. Water (7 to 8 grams) and yellow mercuric oxide (55 grams) were added to this solution. Finally iodine (124 gms.) was added portionwise with constant stirring. Heat was developed and had to be cooled. Stirring was continued till the colour of the iodine disappeared.

The ethereal solution was washed with a concentrated solution of potassium iodide, containing as small quantity of sodium bisulphite to remove the mercuric iodide and traces of iodine which remained. The liquid was dried over anhydrous sodium sulphate or anhydrous calcium chloride. The iodohydrin was removed from the ethereal solution by distillation of the solvent. It remained in the flask as an oil substance, which crystallized on cooling - spontaneously, or by seeding.

Brunel reported that the iodohydrin crystallized in large orthorombic prisms which were colorless. When pure, it was very stable at ordinary temperature and had a very slight odour. It was insoluble in water, soluble in all proportions in benzene, very soluble in alcohol, ether, acetic acid, acetone and chloroform. It melted at 41° - 42.5°C and sublimed in a vacuum at ordinary temperature. It decomposed on heating above 100°C and was steam distilled with slight decomposition.

However on following this method, the oil obtained did not crystallize even after a long period of cooling. 37.2 grams of crude product was obtained.

PREPARATION OF THE IODOHYDRIN OF AMYLENE

Method of Brunel (35)

Amylene (35 grams) was dissolved in ether free of alcohol (150 grams) and treated with water (8 grams), yellow mercuric oxide (55 grams) and iodine (150 grams) as in the method of Brunel (35) used in the preparation of the iodohydrin of cyclohexene.

In this case the colour of the iodine did not disappear with continued stirring. The dark coloured solution was washed several times with a concentrated solution of potassium iodide containing a little sodium bisulphite. Eventually an amber coloured solution was obtained. The ether and unreacted amylene were distilled off on a steam bath, and a very dark red viscous

oil remained. This oil would not crystallize out even after prolonged cooling.

The oil was then distilled under a pressure of 10 mm. A dark oil distilled over and then decomposition of the liquid in the distilling flask occurred and iodine was liberated.

PREPARATION OF THE IODOHYDRIN OF DIHYDRONAPHTHALENE

Method of Leroux (34)

To a solution of dihydronaphthalene (26 grams) in ether (100 grams) was added water (about 4 grams), yellow mercuric oxide (22 grams) and then little by little with constant stirring iodine (50 grams). The reaction had to be carried out with cooling on ice bath. After the absorption of the iodine, the slightly coloured liquid was separated from the mercuric iodide formed during the reaction, washed with a solution of potassium iodide and then finally washed with water. The ether solution, dried with anhydrous sodium sulphate, was concentrated by distilling off two thirds of the ether. The remaining ether in the solution was allowed to evaporate off spontaneously. The crystalline iodohydrin was purified by washing with ether and then recrystallizing from boiling alcohol. It separated as colorless prismatic crystals which melted sharply at 120°C. Progressive heating altered the melting point. This iodohydrin changed rapidly even in darkness. Thus it had to be reacted immediately.

ATTEMPTED PREPARATION OF TETRAHYDRONAPHTHALENE OXIDE

As the iodohydrin of dihydronaphthalene was unstable, an attempt was made to convert the oil to tetrahydronaphthalene oxide.

The oil was dissolved in dry ether. Freshly melted and pulverized sodium hydroxide (3 grams) was added to the cold solution. The reaction mixture was shaken periodically during the space of two days. At the end of this time, the ethereal solution was decanted from the solid and the ether distilled off. A solid separated out from the residual liquid. On purification this solid was identified as naphthalene resulting from the impure dihydronaphthalene from which the iodohydrin was prepared. However, no evidence of the required oxide could be detected.

PREPARATION OF THE CHLOROHYDRIN OF AMYLENE

A saturated solution of calcium hypochlorite (Matheson H.T.H.) was made up and the excess calcium hypochlorite filtered off on a suction pump. A 1 ml. sample of the solution was placed in an erlenmeyer and diluted with water. Potassium iodide solution (10 ml. 10%) was added and the solution then acidified gradually with acetic acid as it was titrated with standard sodium thiosulphate solution using starch as the indicator. The percentage of hypochlorous acid in the solution was calculated and also the amount of this acid necessary to react with the amylene ($\frac{1}{2}$ mole). A 10% excess of the amylene was

used to prevent the formation of dichlorides.

The amylene was then added to the calculated amount of calcium hypochlorite solution in a three-necked flask equipped with stirrer, reflux condenser and dropping funnel. As the mixture was agitated, the acetic acid ($\frac{1}{2}$ mole) was added drop by drop to the solution. The reaction mixture was placed in a salt ice mixture. Stirring was continued for two hours and the mixture was set aside over night. Titration of the solution after standing showed the absence of hypochlorous acid in the solution. The chlorohydrin was separated from the mixture by steam distillation. The aqueous layer of distillate (about 3 to $3\frac{1}{2}$ litres) was saturated with salt and the chlorohydrin extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and the ether removed by distillation. The residual oil was distilled under reduced pressure.

Calculations:-

Standardization of Thiosulphate solution:

Weight of iodine used----- = .2002 grams.

Number of ml. of sodium thiosulphate required in the titration of iodine----- = 15.6 ml.

1 ml. of sodium thiosulphate $\frac{.2002}{15.6}$ gms. of iodine.

.0128 gms. of iodine.

But 126.5 gms. of iodine ----- 26.25 gms. of hypochlorous acid.

.0128 " of " $\frac{.0128}{126.5} \times 26.25$ gms. of hypochlorous acid.

.00266 gms. of hypochlorous acid.

1 ml. of sodium thiosulphate = .00266 grams of hypochlorous acid.

Calculations Continued:-

Calculation of Amylene Chlorohydrin Yield:

Weight of Amylene used ----- = 38.5 gms.

Weight of Hypochlorous acid required ----- = 26 "

1 ml. of Hypochlorous acid solution 30.9 ml. sodium thio-
sulphate.

Percentage Hypochlorous acid in the solution = 8.28%

Volume of Hypochlorous acid solution used--- = 325 ml.

Weight of Acetic acid used ----- = 32 gms.

Weight of Amylene Chlorohydrin obtained = 15.4 grams.
(b.p. 60°- 64°C/10 mm.)

Theoretically 70 grams of Amylene should yield 122.5 grams
of Amylene Chlorohydrin.

Percentage yield = $\frac{15.4}{67} \times 100 = 23\%$.

PREPARATION OF CHLOROHYDRIN OF O-CHLOROCYCLOHEXANOL

A saturated solution of calcium hypochlorite (Matheson H.T.H.) was made up and the excess calcium hypochlorite filtered off on a suction pump. A 1 ml. sample of the solution was placed in an erlenmeyer and diluted with water. Potassium iodide solution (10 ml. 10%) were added and the solution then acidified gradually with acetic acid as it was titrated with standard sodium thiosulphate solution using starch as the indicator. The percentage of hypochlorous acid in the solution was calculated and also the amount of this acid necessary to react with the cyclohexene ($\frac{1}{2}$ mole). A 10% excess of the cyclohexene was used to prevent the formation of dichlorides.

The cyclohexene was then added to the calculated amount of the calcium hypochlorite solution placed in a 500 cc., three-necked flask equipped with stirrer, reflux condenser and dropping funnel. As the mixture was agitated, the acetic acid ($\frac{1}{2}$ mole) was added drop by drop to the solution. As a great deal of heat was produced by the reaction, a salt ice mixture was used for cooling purposes. The mixture was stirred for two hours; then left to stand over night. Titration of a 1 ml. sample showed that no hypochlorous acid remained in the solution. An oily layer separated out on top. The chlorohydrin was separated from the mixture by steam distillation. The aqueous layer of distillate (about $3\frac{1}{2}$ litres) was saturated with salt and the chlorohydrin extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and the ether removed by distillation. The residual oil was distilled under reduced pressure. It began to distill over at 99°C (24 mm.) as a colorless oil and the fraction passing over between 99°C - 105°C was collected. Yield obtained was 21.8 grams.

This procedure was repeated using boric acid in place of acetic acid as the acidifying agent. The yields obtained were less than those obtained by the above method.

ATTEMPTED PREPARATION OF TETRAHYDRONAPHTHALENE OXIDE

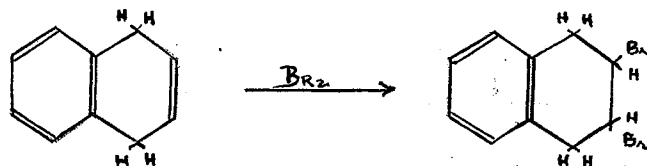
Dihydronaphthalene ($\frac{1}{2}$ mole) was treated with a saturated solution of the calcium hypochlorite as in the previous case of amylene and cyclohexene with the exception that ether (30 ml.) was added to make the dihydronaphthalene more miscible with the hypochlorous acid solution. After the reaction with the hypochlorous acid was over, the ether layer was separated off in a separatory funnel. This solution was then treated with sodium hydroxide, according to the method of Bamberger and Lodter (41) until just basic. The solution was then extracted with ether and dried over anhydrous sodium sulphate. The ether was distilled off leaving an oil. As distillation was continued, a colorless oil distilled over at 60°C and continued to do so as the temperature slowly rose steadily to 205°C. At this point the upward trend of the temperature was slower. A new fraction was collected at this point. The oil coming over in the second fraction solidified in the receiving flask. The temperature rose to 257°C. The product distilling over crystallized to a partially crystallized greenish solid which fumed in the open atmosphere. Time did not permit a purification of this product to be attempted.

CONCLUSIONS AND RECOMMENDATIONS

Difficulty was met in building up a supply of dihydronaphthalene and also in converting it to the chlorohydrin, the intermediate step in the formation of tetrahydronaphthalene oxide. Thus time did not permit the synthesis of 3-oxotetrahydronaphthalene-2-succinic acid to be attempted as was proposed.

There is reason to conclude that tetrahydronaphthalene oxide may be arrived at through the chlorohydrin of 1,4-dihydronaphthalene prepared by the use of high test hypochlorite. Although the volatility of the oxide does give a means of purification, it is felt that the next step in a continuation of the problem would be to purify the 1,4-dihydronaphthalene used in the initial step, in order that accurate determinations of the yield in each step might be accomplished.

The 1,4-dihydronaphthalene would be prepared by either the method of Bamberger and Lodter or that of Scott and Walker using the dimethyl ether of ethylene glycol. 2,3-dibromo-1,4-dihydronaphthalene would then be produced by bromination of the 1,4-dihydronaphthalene.



2,3-dibromo-1,4-dihydronaphthalene could be recrystallized from methanol. Scott and Walker (29) found that the dibromo compound

derived from dihydronaphthalene prepared by their method and recrystallized from methanol had a melting point of 71°C - 71.6°C which corresponds fairly closely with the melting point of 2,3-dibromo-1,4-dihydronaphthalene (71.5°C - 72°C). Following purification, the dibromide would be converted back to 1,4-dihydronaphthalene by the method of Strauss (42) as follows:-

2,3-dibromo-1,4-dihydronaphthalene (12.6 grams) is added all at once to zinc filings (21 grams) covered by absolute alcohol (100 cc.) at 30°C . The reaction soon commences and the temperature rises to about 65°C . The mixture is maintained at 50°C - 65°C till a test portion shows that the dibromide has disappeared. The solution is then decanted from the metal, diluted with water and the oil which is thus precipitated taken up in ether. After washing with brine solution to remove the alcohol, the ethereal solution is dried and evaporated. The residue consists of pure 1,4-dihydronaphthalene melting at 24°C - 25°C , (yield of 5.4 grams).

The chlorohydrin of 1,4-dihydronaphthalene would be prepared by adding gradually acidifying a saturated solution of calcium hypochlorite containing 1,4-dihydronaphthalene.

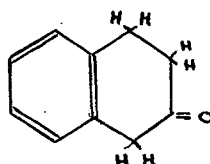
It is felt that it might be advantageous to run a blank saturated solution of calcium hypochlorite, along with the reaction. By titrating samples from each flask over frequent intervals, it would be possible to determine the fall in concentration due to the reaction and that due to a deterioration of the solution. When the fall in concentration of hypochlorous acid in the two flasks became equal over equal

intervals of time, it could be concluded that the reaction was complete.

The product would then be filtered strongly on a suction pump and washed with water and then thoroughly with low boiling ligroin. The chlorohydrin of 1,4-dihydronaphthalene would then be purified by recrystallization from alcohol.

The pure chlorohydrin could then be dissolved in just the necessary quantity of alcohol and treated with a solution of sodium hydroxide. The tetrahydronaphthalene oxide obtained in this manner could be then recrystallized from water if necessary.

Bamberger and Lodter (27) prepared monoketotetrahydronaphthalene



from tetrahydronaphthalene chlorohydrin according to the following procedure:-

Not too large a quantity of tetrahydronaphthalene chlorohydrin (about 15 grams) was heated with 2 to 2½ times the quantity of quinoline in a retort over an oil bath. At about 225°C the brownish yellow solution began to boil. Boiling was continued for eight to twelve minutes and a solid mixture of (water) quinoline, naphthalene and a little ketone distilled over. As soon as effervescence ceased, the retort was placed in position for steam distillation. The

condensate was shaken thoroughly with dilute sulphuric acid to precipitate the naphthalene dissolved in the quinoline, and then extracted with ether. The residue was digested with sodium bisulphite and then repeatedly treated with ether which removed, in addition to the ketone, the aforementioned organic substances. The sulphite solution yielded the ketone as a light brown oil by warming with dilute sulphuric acid. This oil was purified by distilling under reduced pressure. The yield obtained was about 18% theoretical.

By using monoketotetrahydronaphthalene, it might be possible to carry out a similar set of reactions to those done by McRae, Charlesworth, and MacFarlane (7) on cyclohexanone.

BIBLIOGRAPHY

1. McRae, J.A., Charlesworth, E.H., and Alexander, D.S.,
Can. J. Research, B, 21: 1 - 12. 1943.
2. Kendall, E.C., and Osterberg, A.E.,
J. Am. Chem. Soc. 49: 2047 - 2060. 1927.
3. Coffey, S., Rev. trav. Chim. 42: 387 - 436. 1923.
4. Chuang, C.K., and Ma, C.M., Ber. 68: 871 - 876. 1935.
5. Chatterjee, N.N., J. Indian Chem. Soc. 12: 591-594. 1935.
6. Ghosh, R., J. Indian Chem. Soc. 12: 601 - 603. 1935.
7. Charlesworth, E.H., McRae, J.A., and McFarlane, H.M.,
Can. J. Research, B, 21: 55 - 64. 1943.
8. Openshaw, H.T., and Robinson, R., J. Chem. Soc. 941-946. 1937.
9. Haworth, R.D., and Mavin, C.R., J. Chem. Soc. 1012-1016. 1933.
10. Fisher, E., and Zemplén, G., Ber. 42: 4878 - 4892. 1909.
11. McKenzie, A., and Wren, H., J. Chem. Soc. 97: 1355-1359. 1910.
12. Kotz, A., and Stalman, G., J. prakt. Chem. 68: 156-173. 1903.
13. Conrad, M., and Bischoff, C.A., Ann. 214: 68 - 72. 1882.
14. Finkelstein, H., Ber. 43: 1528 - 1532. 1910.
15. Conrad, M., and Bruckner, C., Ber. 24: 2993 - 3005. 1891.
16. Curtis, R.S., Am. Chem. J. 19: 691 - 701. 1897.
17. Wallach, O., and Evans, E., Ann. 360: 44 - 50. 1908.
18. Wallach, O., and Haworth, W.N., Ann. 389: 188-194. 1912.
19. Wallach, O., and Isaac, E., Ann. 347: 328-377. 1906.
20. Auwers, K., and Ellinger, P., Ann. 387: 200-239. 1911.
21. Boehringer, C.H., Sohn, A.G., Brit. Pat. 378,095, Aug. 8, 1932.
Chem. Abstracts 27: 3945. 1933.
22. Kohler, E.P., Heritage, G.L., and MacLeod, A.L.,
Am. Chem. J. 46: 217 - 236. 1911.
23. Iyer, B.H., J. Indian Chem. Soc. 17: 215 - 218. 1940.

Bibliography Continued

24. McRae, J.A., Charlesworth, E.H., Archibald, F.R., and Alexander, D.S., Can. J. Research, B. 21: 186-193. 1943.
25. Traube, W., and Lehmann, E., Ber. 32: 720 - 721. 1899.
26. Traube, W., and Lehmann, E., Ber. 34: 1971-1983. 1901.
27. Bamberger, E., and Lodter, W., Ann. 288: 75. 1895.
28. Schlenk, Ann. 463: 91.
29. Scott, N.D., Walker, J.F., and Hansley - 2nd and Eng. Chem. 32, No.3, 314. 1940. United States Patent Office 2,108,213.
30. Clarke, H.T., J. Chem. Soc. 101: 1802. 1912.
31. Capinjola, J. Am. Chem. Soc. 67: 1615. 1945.
32. Bamberger, E., and Lodter, W., Ber. 26: 1833 - 1844. 1893.
33. Detoef, A., Bull. Soc. Chim. Mem. (Ser. 4) 31: 102 - 108. 1922.
34. Leroux, H., Ann. Chem. and Phys. Ser. 21, 507. 1910.
35. Brunel, I., Ann. Chem. and Phys. Ser. 8, Vol. 6, 219. 1905.
36. N.V. de Bataafsche Petroleum Maatschappij - Fr., 769,404 - Aug. 25, 1934. C.A. 29, 476. 1935.
37. Pedro Sanchez, C.A. 32, 3559 (1938).
38. Fortey, J. Chem. Soc. 23: 948. 1898.
39. Coleman, G.H., and Johnstone, H.F., Organic Synthesis 5, 31.
40. C.A. 33, 6533 (1939)
J. Ourisson and M. Kastner, Congr. Chim. Ind. comp. rend. 18 me Congr., Nancy, Sept., Oct., 1938 - 983-991.
41. Bamberger, E., and Lodter, W., Ann. 287 - 288. p.89.
42. Strauss, Ber. 46, 1054. 1913.
43. Lippert, Ann. 276, 171. 1893.
44. Strauss, F., and Lemmel, L., Ber. 46: 232 - 241. 1913.
45. Wohl and Schweitzer, Ber. 40, 94. 1907.
46. Bamberger, E., and Lodter, W., Ber. 24: 1887 - 188.
47. Soc. Dyers and Colourists 62, 57, Feb. 1946.
Brit. Pat. 571,266.