

CVI.—*Electrolytic Reduction. Part VI. Unsaturated Aldehydes and Ketones.*

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THE compounds hitherto submitted to electrolytic reduction have been confined entirely to the aromatic series. Distinct relations have been established, and it has been proved repeatedly that the rate of reduction of aromatic aldehydes and ketones diminishes as the potential of reduction is lowered; thus benzaldehyde is reduced much more readily with lead cathodes than with copper, but at the same time the supertension of lead is much higher than that of copper. It has been shown, further, that the position of substituted groups in the benzene nucleus greatly influences the nature

of the reduction product. The significance of the latter relation is not clear, and the present work was undertaken in order to obtain a more intimate knowledge of the reactions taking place. It was hoped that a comparative study of aliphatic and alicyclic ketones and aldehydes would throw a considerable amount of light on the nature of the benzene nucleus. Many compounds were investigated, but the complicated nature of the reduction products rendered it necessary considerably to curtail the scope of the work. The following experiments are confined chiefly to an investigation of the products of reduction of aldehydes and ketones on lead cathodes.

EXPERIMENTAL.

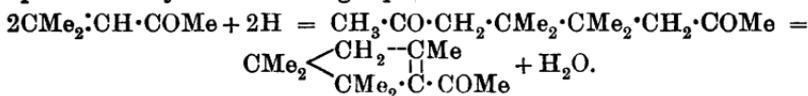
Crotonaldehyde.

The reduction products of crotonaldehyde have been studied previously. The chief substance formed is butyl alcohol. The electrolytic method gave practically the same result in acid medium. Twenty-five grams of crotonaldehyde, 50 c.c. of alcohol, 150 c.c. of water, and 10 grams of sulphuric acid were reduced in the apparatus already described (*Trans.*, 1906, **89**, 1512), but the precaution was taken to close the porous pot with a stopper fitted with a reflux condenser. This was necessary as the products were of a volatile nature. A sheet lead cathode was used measuring 75 sq. cm. on one side, and a current of 2 amperes for eight hours. The reaction mixture was diluted with water, extracted with ether, the solution dried and fractionated. Seventy per cent. of the product boiled below 120°, 20 per cent. boiled at 190—230°, and a small residue was left in the distilling flask. The total yield of reduced substances weighed 22 grams. The remainder was lost along with the evolved hydrogen at the cathode. The fraction of low boiling point was composed almost entirely of *n*-butyl alcohol. The fraction boiling at 190—230° was a mixture, and was not studied further.

Mesityl Oxide.

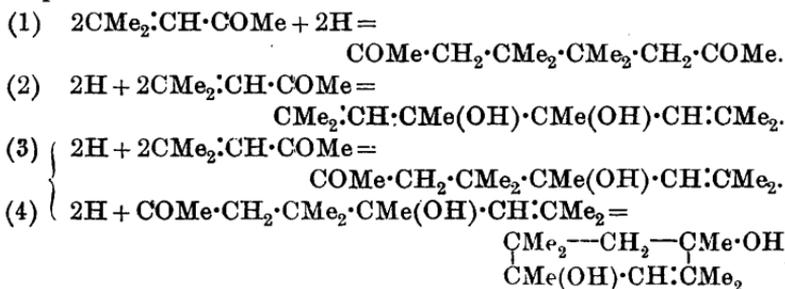
Many attempts have been made to follow the course of reduction of mesityl oxide and isolate definite products from the reaction mixture. The experiments have been conducted chiefly in alkaline media, and the products have probably been similar in all cases. Baeyer (*Annalen*, 1866, **140**, 290) first examined a liquid product, to which he assigned the formula $C_{12}H_{22}O$. Claisen (*Annalen*, 1876, **180**, 7) re-investigated and named the reduced compound deoxymesityl oxide, to which the formula $C_{12}H_{20}O$ was given. The above researches were conducted with a mixture, and no substance of constant boiling point was isolated. A more recent investigation

has been carried out by Harries and Hübner (*Annalen*, 1897, **296**, 295), and an attempt made to elucidate the constitution of deoxymesityl oxide. The reaction is assumed to take place in stages represented by the following equations:



The first step represents the reduction reaction, and the second an inner condensation due to the nature of the medium. These facts are supported by the formation of an oxime, $\text{C}_{12}\text{H}_{20}\text{:NOH}, \text{H}_2\text{O}$, and an oxidation product identical with tetramethylsuccinic acid. The pure compound was not isolated. A different method of reducing mesityl oxide was carried out by Kerp and Müller (*Annalen*, 1894, **290**, 132). The chief product was an alcohol, $\text{C}_8\text{H}_{14}\text{O}$, with a smaller quantity of an oil containing 73.44 per cent. of carbon and 12.16 per cent. of hydrogen, but boiling at approximately the same temperature as deoxymesityl oxide. The compound, $\text{C}_{12}\text{H}_{20}\text{O}$, however, contains 80 per cent. of carbon, whereas the new oil is remarkable for its high percentage of oxygen. The correctness of Harries and Hübner's view was therefore open to some doubt, especially as the oxime mentioned above corresponded with a ketone of the formula $\text{C}_{12}\text{H}_{20}\text{O}, \text{H}_2\text{O}$ ($\text{C}_{12}\text{H}_{22}\text{O}_2$). Furthermore, these authors apparently assumed that the compound in their hands was identical with Claisen's deoxymesityl oxide without the support of analysis. It seemed possible, therefore, that the mixture in the hands of Harries and Hübner contained at least one substance of the formula $\text{C}_{12}\text{H}_{22}\text{O}_2$, from which the oxime was derived, and that the compound $\text{C}_{12}\text{H}_{20}\text{O}$ was due to decomposition of the compound $\text{C}_{12}\text{H}_{22}\text{O}_2$ or some similar substance. The compound $\text{C}_{12}\text{H}_{20}\text{O}$ was probably formed during repeated fractionation of an original reduction product of the formula $\text{C}_{12}\text{H}_{22}\text{O}_2$. This view was entirely confirmed by the experiments described below. Mesityl oxide was reduced by the electrolytic method, but under conditions as nearly as possible like those described in the work of Harries and Hübner. The product boiled almost entirely at 215—235°, and yielded an oxime identical with that described by Harries and Hübner. It was probably the same mixture as that in the hands of the latter investigators. The formula agreed, however, with $\text{C}_{12}\text{H}_{22}\text{O}_2$. When fractionated, it lost water even under diminished pressure, and was gradually resolved into two products of the formulæ $\text{C}_{12}\text{H}_{20}\text{O}$ and $\text{C}_{12}\text{H}_{22}\text{O}_2$. The latter was a solid, and was obtained quite pure. It readily yielded the oxime already mentioned above. It was saturated, and on oxidation gave an acid identical with tetramethylsuccinic acid. It was stable towards heat, and could be

fractionated unchanged, even at atmospheric pressure. It probably had the constitution $\text{COMe}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{COMe}$. The original reduction product, on the other hand, was highly unsaturated, as was also the compound $\text{C}_{12}\text{H}_{20}\text{O}$, and readily lost water when heated. These facts can be supported best by assuming that at least two of the reactions indicated in the following equations take place:



Reduction was carried out in the apparatus already described (*loc. cit.*). Several preliminary experiments were conducted with lead cathodes in order to determine the best working conditions. Both acid and alkaline electrolytes were tried, and were found to exercise a considerable influence on the products of the reaction. Sulphuric acid electrolytes, however, had to be abandoned as the lead of the cathode passed into solution during reduction. The product was a heavy, red oil containing a considerable percentage of lead, but mixed with the better known deoxymesityl oxide. The red oil was easily hydrolysed when boiled with water, leaving a residue of lead hydroxide. A similar reaction took place with many other aliphatic and alicyclic compounds, but the product was in no case investigated further than described above. This curious behaviour of lead cathodes was noticed only in acid solutions, and never in alkaline ones. No similar reaction was detected with copper. The concluding experiments were therefore conducted in alkaline media. The mixture in the cathode cell contained 25 grams of mesityl oxide, 50 c.c. of water, 160 c.c. of alcohol, and 13 grams of potassium hydroxide. A current of 6 amperes was used for five hours. The electrodes had an area of 75 sq. cm. on one side. The temperature rose somewhat as reduction proceeded, and was usually 10° higher than the surrounding atmosphere at the end of the experiment. The product was diluted with water, and the oil extracted with ether. The ethereal extract was dried, and, after the removal of the ether, fractionated under 20 mm. pressure. The following fractions were obtained: (I) b. p. below 93° , 5 grams; (II) b. p. $93\text{--}110^\circ$, 2.5 grams; (III) b. p. $110\text{--}130^\circ$, 10 grams. There was also a small residue of higher boiling point. The quan-

tities of these fractions varied somewhat in different experiments, but in every case there was a loss of material amounting to about 20 per cent. of the mesityl oxide used. This loss was finally traced, and was found to be due to the formation of highly volatile products which disappeared during manipulation. An easy method of preparing these fractions of low boiling point was discovered later, and will be dealt with elsewhere.

Fraction I was composed chiefly of unchanged mesityl oxide and a saturated ketone identical with methyl isobutyl ketone. The quantity of the latter substance was never very considerable. It yielded a semicarbazone melting at 134°.

Fractions II and III were mixed and boiled at 210—230°/760 mm., with partial decomposition:

0·1278 gave 0·3437 CO₂ and 0·1307 H₂O. C=73·34; H=11·19.

C₁₂H₂₂O₂ requires C=72·72; H=11·11 per cent.

C₁₂H₂₀O „ C=80·00; H=11·1 „ „

This mixture therefore contained chiefly compounds of the formula C₁₂H₂₂O₂. Water was easily eliminated on distillation, either under diminished or the ordinary pressure. Decomposition was not complete, however, even after boiling for many hours. An attempt was made to isolate pure constituents from the above mixture by fractionation under diminished pressure. This operation was carried out thirty times, and two main fractions were obtained boiling at 107—108°/20 mm. and 122—123°/20 mm. respectively. Neither fraction was quite pure, but they had the approximate formulæ C₁₂H₂₀O and C₁₂H₂₂O₂ respectively.

The fraction boiling at 122—123°/20 mm. deposited, after some time, well defined crystals readily soluble in the usual organic solvents. These melted sharply at 53—55°, and were quite pure:

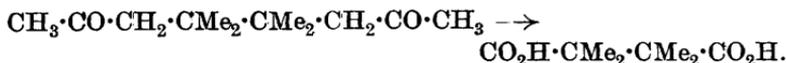
0·1025 gave 0·2730 CO₂ and 0·1060 H₂O. C=72·63; H=11·49.

C₁₂H₂₂O₂ requires C=72·72; H=11·11 per cent.

These crystals were quite stable towards heat, and could be distilled without decomposition. They readily yielded an oxime (m. p. 156—157°) identical with that prepared by Harries and Hübner from deoxymesityl oxide. This oxime was converted into the hydrochloride melting and decomposing at 120—125°, which is in agreement with the records of previous investigators.

A small quantity of the original ketone was oxidised by means of chromium trioxide in the manner described by Harries and Hübner. An acid was obtained melting at 190° with effervescence due to the liberation of carbon dioxide. This substance appeared

to be identical with tetramethylsuccinic acid. It was formed probably by decomposition according to the following scheme:



The formula of the substance $\text{C}_{12}\text{H}_{22}\text{O}_2$ is therefore well established. The original crystals decolorised bromine only very slowly with the liberation of hydrogen bromide. They formed a mono-semicarbazone on long keeping in contact with the necessary reagents in the cold. A white, crystalline product was formed, crystallising from benzene and melting at 185—186°:

0·1026 gave 0·2271 CO_2 and 0·0905 H_2O . C=60·36; H=9·80.

$\text{C}_{13}\text{H}_{25}\text{O}_2\text{N}_3$ requires C=60·11; H=9·88 per cent.

It was notable that only one carbonyl group reacted with either hydroxylamine or semicarbazide even on long contact with these reagents.

Numerous attempts were made to find a solvent suitable for crystallising the compound melting at 53—55°. This, however, failed on account of the ready solubility in all the ordinary organic reagents.

The second fraction referred to above and boiling at 107—108°/20 mm. was fractionated under the atmospheric pressure, and lost a further quantity of water. It boiled at 218—220°/760 mm. (Found, C=79·86; H=11·57. $\text{C}_{12}\text{H}_{20}\text{O}$ requires C=80·00; H=11·11 per cent.)

This substance, therefore, was deoxymesityl oxide in a fairly pure state. It readily absorbed bromine without the liberation of hydrogen bromide, and was therefore unsaturated. An iodine determination was made in the usual manner, when 0·3 gram of deoxymesityl oxide absorbed 30 c.c. of *N*/5-iodine solution. This corresponds with nearly two molecules of iodine per molecule of the original oil. Deoxymesityl oxide was allowed to remain in contact with an aqueous solution of semicarbazide hydrochloride and sodium acetate for several months, when a solid substance was slowly formed. This was crystallised several times from benzene, and was finally separated into two compounds melting respectively at 137° and 161°, the latter being the less soluble:

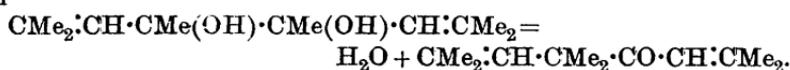
0·1014 gave 0·2440 CO_2 and 0·0892 H_2O . C=65·63; H=9·87.

$\text{C}_{13}\text{H}_{23}\text{ON}_3$ requires C=65·82; H=9·70 per cent.

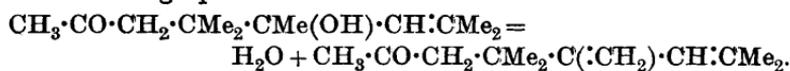
This substance therefore was the *monosemicarbazone* of deoxymesityl oxide. The compound melting at 137° was difficult to obtain pure, and sufficient was not prepared for a complete analysis. There is probably a third solid substance formed, but this was

never isolated in a pure state. Deoxymesityl oxide was readily attacked by oxidising agents, but yielded no well defined products. Tetramethylsuccinic acid was not produced.

The most probable explanation of the formation of deoxymesityl oxide is that the reaction takes place in two stages. Mesityl oxide is first reduced at the carbonyl group according to equation 2. The product, like many others of a similar nature, readily loses water when heated, and becomes converted into a ketone on similar lines to the pinacone-pinocolin transformation, and represented in an equation as:



There is, however, the second possibility that the reduction takes place as in equation 3; the product then loses water on distillation, and leads to the introduction of a second double linking, as in the following equation:



Methylheptenone (Natural).

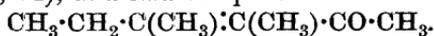
The above product was the naturally occurring oil, to which the formula $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ has been assigned. The reduction products have been investigated previously by Wallach (*Annalen*, 1893, **275**, 171), who isolated an unsaturated alcohol as the only product. A few preliminary experiments were conducted with the electrolytic method of reduction in order to determine the best working conditions. It was soon found that reduction proceeded very slowly in alkaline solution, even when lead cathodes were used, and the method was abandoned. Sulphuric acid was next tried as electrolyte, when reduction proceeded smoothly and regularly. The product was deep red, and always contained some lead dissolved in it. This lead compound was not isolated in a pure state. The experiment was carried out in the following manner: A mixture of 50 grams of methylheptenone, 150 c.c. of alcohol, and 50 c.c. of 25 per cent. sulphuric acid were reduced, employing a current of 1.5 amperes for twenty-four hours. A lead cathode was used measuring 75 sq. cm. on one side. The whole mixture was then distilled in a current of steam, the distillate extracted with ether and the ethereal solution dried. On removal of the ether a product was obtained amounting to 45 per cent. of the original compound taken. The non-volatile portions left in the distilling flask deposited lead hydroxide. The non-volatile liquid portion weighed 35 per cent. of the methylheptenone reduced. There was

always a loss of material of 15 per cent. The volatile portion was fractionated, and yielded two main parts boiling at 110—150° and 150—200° in the proportion of 4:9. The latter was treated with a concentrated solution of sodium hydrogen sulphite to separate the unchanged methylheptenone, and the residual oil refractionated. A product was then isolated boiling at 174—176°/760 mm., and identical with methylheptenol. The fraction of low boiling point was treated in a similar manner, when two main fractions were obtained boiling respectively at 118—125° and 125—135°. The latter on refractionation yielded a product boiling at 127—129° identical with the compound $\text{CH}_2 \begin{matrix} \text{CH}_2 - \text{CH} \cdot \text{CHMe}_2 \\ \text{CHMe} \cdot \text{O} \end{matrix}$ previously prepared by Wallach by the action of dilute sulphuric acid on methylheptenol. The portion of lower boiling point yielded a fraction boiling at 120—123°, which was evidently a mixture of the above inner ether and a substance rich in carbon, probably an unsaturated hydrocarbon. This hydrocarbon was never isolated in a pure state, but fractions were obtained which readily decolorised bromine, and were readily attacked by cold solutions of potassium permanganate.

The non-volatile portion left over from the steam distillation was also fractionated, but readily decomposed, depositing large quantities of lead compounds. It yielded no product of constant boiling point.

Dimethylmesityloxiide.

This substance was prepared by the method already described (Proc., 1907, **23**, 74), and had the probable constitution



It is related to methyl ethyl ketone in exactly the same manner as acetone to mesityl oxide. It was reduced and worked up in the same way as in the case of mesityl oxide. The product was fractionated, when the following main portions were obtained under 15 mm. pressure: (I) b. p. 40—95°, 30 per cent.; (II) 145—165°, 45 per cent.; (III) 165—175°, 25 per cent.

Fraction I boiled completely at 160—170°; it had a strong odour of peaches, and contained a considerable amount of unchanged product. It readily yielded a semicarbazone, and thus differed from the parent substance. A small quantity was isolated and crystallised from benzene, when it melted at 125—130°:

0.1015 gave 0.2200 CO₂ and 0.0852 H₂O. C=59.11; H=9.33.

C₉H₁₇ON₃ requires C=59.01; H=9.29 per cent.

Reduction therefore had taken place at the double linking to produce a saturated ketone. The quantity present was small, and

did not permit of further investigation. The compound analysed was probably a mixture of two isomeric semicarbazones.

Fractions II and III were treated together. They were redistilled and separated into two main portions boiling respectively at 135—138°/15 mm. and 172—173°/15 mm., but at the same time a considerable amount of water was eliminated. The fraction of lower boiling point was redistilled under the atmospheric pressure, when it boiled chiefly at 250—260°, but still lost water. A fraction was finally obtained boiling at 254—256°, which gave the following results on analysis:

0.1367 gave 0.4090 CO₂ and 0.1490 H₂O. C=81.67; H=12.11.

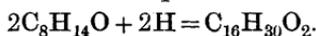
C₁₆H₂₈O requires C=81.35; H=11.86 per cent.

The fraction boiling at 172—173°/15 mm. was by far the larger, and on analysis gave the following results:

0.1550 gave 0.4300 CO₂ and 0.1673 H₂O. C=75.61; H=11.98.

C₁₆H₃₂O₂ requires C=75.59; H=11.90 per cent.

The reduction of dimethylmesityl oxide had proceeded, therefore, in practically the same manner as mesityl oxide itself. The main course of the reaction took place according to the equation:



The product C₁₆H₃₀O₂ was a mixture of at least two compounds, one stable and the other unstable at the boiling point. The latter lost water on distillation, and yielded a substance of lower boiling point, C₁₆H₂₈O, which was then stable at its boiling point.

Citronellaldehyde.

This substance was extremely difficult to reduce, even when lead cathodes were employed. Electrodes of the highest known super-tension were employed, namely, amalgamated lead or zinc, but even then reduction took place so slowly that the investigation was abandoned.

Citral.

The reduction products of citral have been recently investigated by two authors. Verley (*Bull. Soc. chim.*, 1899, [iii], **21**, 409) obtained chiefly a complex substance of high boiling point (203—205°/15 mm.), to which he assigned the pinacone formula, C₉H₁₅·CH(OH)·CH(OH)·C₉H₁₅. Skita (*Ber.*, 1909, **42**, 1635) obtained a crystalline substance in a pure state. It was expected that one of these compounds would be produced by the electrolytic method of reduction. The experiments were conducted with citral obtained from lemon-grass oil by fractionation, and was

probably a mixture of two closely allied aldehydes. Reduction was first carried out in alkaline solution, and a viscid, oily substance was obtained as sole product, but identical with that produced in the concluding experiments. The reaction was finally carried out in the presence of sulphuric acid, when a variety of products was isolated.

The cathode solution contained 25 grams of citral, 150 c.c. of alcohol, 50 c.c. of water, and 20 grams of sulphuric acid. A lead cathode of 75 sq. cm. superficial area on one side was used, and a current of 2.5 amperes for twelve hours. The current, however, fell off considerably as the experiment proceeded, and was usually 0.5 ampere at the finish. Twenty ampere-hours were supplied for each experiment. The product was usually red, and contained considerable quantities of dissolved lead. It was distilled in a current of steam, and the volatile portion extracted with ether and finally fractionated. A small quantity of water eliminated during distillation, and a mixture of hydrocarbons was obtained, boiling at 165—185°. This could not be divided into pure constituents, but corresponded in formula with anhydrogeraniol. The remainder boiled at 210—235°, and was a mixture of at least two alcohols. The main fraction boiled at 217—220°, and on analysis yielded the following results:

0.1024 gave 0.2940 CO₂ and 0.1082 H₂O. C=78.10; H=11.64.

C₁₀H₁₈O requires C=77.92; H=11.69 per cent.

This substance therefore was isomeric with geraniol. It was fairly stable towards heat, but decomposed slowly at its boiling point with loss of water and the formation of the above hydrocarbons. It readily lost water when treated with most reagents even in the cold, with the formation of the above mixed hydrocarbons. Sodium hydrogen sulphite solution, phthalic anhydride, phosphorus penta- and tri-chlorides all split off water. Diphenyl-carbamyl chloride and pyridine on the water-bath caused the same decomposition, but at the same time a small quantity of a solid melting at 82° was formed, which indicated the presence of geraniol. It seemed probable, therefore, that two alcohols were present, one of which was the known geraniol, but the main portion was an unstable isomeric alcohol boiling at about 220°. This was never obtained quite pure on account of its unstable nature.

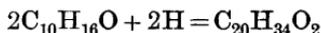
The non-volatile portion left in the steam distillation flask was extracted with ether and fractionated. It boiled at 210—280°/25 mm., the main portion being obtained at 216—220°/25 mm. The latter was isolated, and on analysis gave the following results:

0·1048 gave 0·3138 CO₂ and 0·1054 H₂O. C=81·68; H=11·11.

C₂₀H₃₄O₂ requires C=78·43; H=11·11 per cent.

C₂₀H₃₂O ,, C=83·33; H=11·11 ,, ,,

Reduction, therefore, had probably proceeded according to the equation:



in a manner similar to that occurring in the case of mesityl oxide. The compound C₂₀H₃₄O₂ then lost water when fractionated, and became partly converted into the compound C₂₀H₃₂O. The compound C₂₀H₃₄O₂ was probably the same as that obtained by Verley, and of the nature of a pinacone. It was highly unsaturated and without aldehydic properties. It was unstable towards heat, and lost water when distilled. The compound described by Skita was not present.

Menthone.

This substance has been previously investigated by Beckmann (*J. pr. Chem.*, 1897, [ii], 55, 18 and 30), who obtained a mixture of menthol and menthopinacone on reduction with sodium. It was expected that the same products would be obtained by the electrolytic method which was tried, using an alkaline electrolyte. Reduction, however, proceeded very slowly, even when lead cathodes were used. The acid medium was next tried, and satisfactory results were obtained. Reduction proceeded readily, and was soon complete. Twenty-five grams of menthone, 150 c.c. of alcohol, 50 c.c. of water, and 10 grams of sulphuric acid were treated. A lead cathode was used, measuring 75 sq. cm. on one side. A current of 2 amperes was passed through this mixture for twelve hours (overnight). The product was distilled in a current of steam, and the volatile portion extracted with ether. The distillate was composed chiefly of menthol, and amounted to 82 per cent. of the original menthone. The viscid, oily residue in the steam distillation flask was allowed to remain for several days, when it deposited large, colourless crystals. These were separated by filtration, and amounted to 10 per cent. of the total product. They crystallised from alcohol in large cubes closely resembling sodium chloride in appearance. These crystals could easily be obtained quite perfect in shape, and with sides 5 cm. long. They melted at 172—173°:

0·1016 gave 0·2873 CO₂ and 0·1140 H₂O. C=77·12; H=12·46.

C₂₀H₃₈O₂ requires C=77·42; H=12·26 per cent.

A second crop of crystals melting at 148—150° was obtained from the mother liquors:

0.1004 gave 0.2848 CO₂ and 0.1120 H₂O. C=77.36; H=12.39.

These two substances therefore were isomeric menthopinacones, but neither was identical with the one described by Beckmann (*loc. cit.*), which melted at 94°. The quantity of material in hand was small, and further experiments were not undertaken as the results agreed with past experience.

Carvone.

Carvone has been carefully investigated by many authors, and a variety of well defined reduction products has been isolated. Reaction takes place generally at the double link in the ring, and two main products are obtained, namely, dihydrocarvone and α -dicarvelone. The double link in the side-chain does not appear to be readily attacked, and usually persists in the reduction product. The product of electrolytic reduction was similar to those already recorded, and differed chiefly in the formation of a much larger percentage yield of dicarvelone.

The carvone used in the following experiments was obtained from the oil of caraway. It was purified by conversion into the hydrosulphide. The latter was crystallised in the usual manner, and melted at 212°, considerably higher than previously recorded. The liberated carvone boiled at 225°, and had α_D^{18} 61.035". It was therefore quite pure, a fact confirmed by analysis. The pure carvone was easily reduced in both acid and alkaline solutions, and the concluding experiments were conducted in the latter medium to avoid the formation of products containing lead.

The cathode solution contained 50 grams of carvone, 100 c.c. of water, 200 c.c. of alcohol, and 18 grams of potassium hydroxide. Lead cathodes were employed, measuring 75 sq. cm. on one side. The current was 3 amperes at the beginning of each experiment, but fell to 0.5 ampere at the finish. Each experiment was allowed to proceed for twelve hours (overnight), when a semi-solid product was formed. The crystals were removed by filtration, and the oily filtrate allowed to remain for several weeks to deposit more of the solid. The total yield of the latter amounted to 50 per cent. of the carvone taken. The oily residue was extracted with ether, and fractionated under diminished pressure. Practically the whole product distilled at 280—290°/70 mm. It was a viscid, colourless oil, and appeared identical with that previously recorded (Harries, *Ber.*, 1899, **32**, 1316). It was refractionated, and boiled at 260—262°/40 mm. Similar experiments conducted with sulphuric acid as electrolyte and a much larger percentage of the oil was obtained (90—95 per cent.) at the expense of the crystals.

The solid compound obtained above was crystallised from alcohol and melted at 150—151°, which is slightly higher than that previously recorded. It was obtained in large, flat prisms, which could easily be grown to a considerable size. It appeared to be identical with α -carvelone. The mother liquor deposited a further crop of crystals on keeping, which proved to be a mixture of two compounds, the one described above and a second compound forming diamond-shaped crystals. These were separated by allowing an alcoholic solution to evaporate slowly, when large crystals were produced and separated mechanically. The new substance melted at 149—150°, which is practically the same as for α -carvelone. The two compounds were analysed, and yielded the following results:

(1) M. p. 150—151°:

0.1000 gave 0.2910 CO₂ and 0.0900 H₂O. C=79.36; H=10.00.

(2) M. p. 149—150°:

0.1002 gave 0.2914 CO₂ and 0.0904 H₂O. C=79.31; H=10.02.

C₂₀H₃₀O₂ requires C=79.47; H=9.93 per cent.

These two substances were therefore isomeric. α -Carvelone is slightly levorotatory, and yields an oxime melting at 228°, which is somewhat higher than previously recorded. The new compound is slightly dextrorotatory, and yields an oxime melting at 171—173°. The latter is very soluble in alcohol or benzene, but insoluble in light petroleum. It was purified by recrystallisation from a mixture of alcohol and water, but did not melt sharply:

0.1006 gave 0.2654 CO₂ and 0.0940 H₂O. C=71.94; H=10.38.

C₁₀H₁₆ON requires C=72.29; H=9.64 per cent.

It was therefore the dioxime of the new carvelone, but in a slightly impure state. The two carvelones above mentioned are not stereoisomerides. A mixture of equal quantities of each forms an inactive product melting at 121°, which happens to be the same as racemic α -carvelone. The oxime, however, of the mixed carvelones has not a sharp melting point, and is not identical with the oxime of racemic carvelone (m. p. 287°). These two compounds therefore appear to be structurally different.

The oily product referred to above deposited a further crop of crystals on long keeping, and could not be obtained in a pure state.

Pulegone.

The reduction products of pulegone have been studied by many investigators. Tiemann and Schmidt (*Ber.*, 1896, 29, 914)

isolated pulegol, and Beckmann and Pliessner (*Annalen*, 1891, **262**, 30) obtained menthol as a final product. The reaction in both cases took place most readily at the ketone group. Harries and Roeder (*Ber.*, 1899, **32**, 3367) obtained a bimolecular reduction product, 10 per cent. of which was crystalline and melted at 118—119°. The latter substances probably had the pinacone structure in consideration of the easy reducible nature of the carbonyl radicle. Past experience has shown, however, that reduction frequently takes place at both the double linking and the carbonyl group simultaneously. It is notable that menthone was not produced in any considerable quantity, although it is fairly stable towards alkaline reducing agents.

The first experiments tried by the electrolytic method were conducted in alkaline medium. Thirty grams of pulegone, 150 c.c. of alcohol, 100 c.c. of water, and 15 grams of potassium hydroxide were treated overnight (twelve hours), a current of 2 amperes being used. The cathode measured 75 sq. cm. on one side, and was composed of sheet lead. The product was distilled in a current of steam. The volatile portion weighed 10 grams, and was pure menthone. The residue in the distilling flask was extracted with ether, dried, and allowed to remain exposed to the air for several days. Crystals were deposited, which were collected and recrystallised from alcohol. These melted sharply at 119°, and were identical with those described by Harries and Roeder (*loc. cit.*). They were entirely devoid of ketonic properties, and had the formula $C_{20}H_{34}O_2$. They were probably pulego-pinacone. A second substance was also obtained, melting at 148°. This appeared to be the mentho-pinacone described above, but the quantity was too small to investigate further. The residual oil remained liquid, even on long keeping. It was of an unreactive character, and was not investigated further. It constituted the bulk of the non-volatile portion.

A second reduction experiment was conducted, in which sulphuric acid replaced potassium hydroxide as electrolyte. The product was treated exactly as before. The volatile portion weighed 14 grams, and was a mixture of menthol and menthone. The latter was removed as the semicarbazone, and the former obtained as a liquid boiling at 214—216°. The relative quantity of each varied somewhat, but the main portion was menthol. The non-volatile portion was similar in character to that already described. It would appear, therefore, that pulegone follows the usual rule on reduction. The reaction proceeds at both the double linking and the carbonyl group simultaneously.

Cinnamaldehyde.

This substance readily resinifies on reduction in both acid and alkaline medium. The reaction was therefore tried in a nearly neutral electrolyte (Trans., 1911, **99**, 1114). Five grams of cinnamaldehyde, 25 c.c. of alcohol, 20 c.c. of ethyl acetate, 20 c.c. of water, and 4 grams of potassium acetate were electrolysed with a current of 1 ampere for three hours. A lead cathode was employed, and a current density of 0.05 amperes per sq. cm. The product was diluted with water, extracted with ether, dried, and fractionated under diminished pressure. Two fractions were obtained, namely, (I) b. p. 100—200°/25 mm., and (II) b. p. 200—300°/25 mm. There was also a portion of higher boiling point. Fraction I was treated with a solution of sodium hydrogen sulphite to remove the unchanged aldehyde. The residue boiled at 235°/760 mm., and was β -phenylpropyl alcohol, the yield being 55 per cent. Fraction II could not be identified. The following results were obtained in three parallel experiments:

Cathode material	Copper	Lead	Lead
Temperature	20—30°	20—30°	40—50°
β -Phenylpropyl alcohol...	20 per cent.	55 per cent.	25 per cent.
High boiling fraction	60 ,,	20 ,,	40 ,,

These results agree substantially with those previously recorded (*loc. cit.*).

Styryl Methyl Ketone.

Harries and Hübner have already studied the reduction products of this substance (*Annalen*, 1897, **296**, 295). These authors found it necessary to conduct the reaction in a neutral medium to avoid the excessive formation of resins. The products were benzylacetone, and the bimolecular compound dibenzylidiacetone. The electrolytic method yielded similar results. A resinous, semicrystalline product was formed in both acid and alkaline media, and the concluding experiments were conducted in the almost neutral electrolyte (*loc. cit.*). The cathode compartment contained 5 grams of styryl methyl ketone, 15 c.c. of ethyl acetate, 30 c.c. of alcohol, 30 c.c. of water, and 4 grams of potassium acetate. A current of 1 ampere was used, and reduction was complete in four hours. The product was extracted with ether, dried, and distilled. Two fractions were obtained, namely, (I) b. p. 140—160°/30 mm., and (II) b. p. 240—260°/30 mm. There was also a portion of higher boiling point. Fraction I was benzylacetone, and boiled at 235°/760 mm. Fraction II solidified on cooling, and melted at 161°. This was

the dibenzylidiacetone previously recorded (*loc. cit.*). The following results were obtained in two experiments:

Cathode material.....	Copper	Lead
Temperature.....	20—30°	20—30°
Benzylacetone	55 per cent.	75 per cent.
Dibenzylidiacetone	35 ,,	20 ,,

p-Methoxystyryl Methyl Ketone.

The above substance was reduced by Harries and Hübner (*loc. cit.*) in the manner already described. The products were anisylacetone and dianisylidiacetone. The electrolytic method yielded similar results. Five grams of *p*-methoxystyryl methyl ketone, 20 c.c. of ethyl acetate, 35 c.c. of alcohol, 20 c.c. of water, and 4 grams of potassium acetate were treated exactly as in the previous experiment. The products were an oil boiling at 277°/760 mm., and a solid melting at 151—152°. These were respectively anisylacetone and dianisylidiacetone. There was also a product of higher boiling point. The results of comparative experiments are given below:

Cathode material.....	Copper	Lead
Temperature.....	20—30°	20—30°
Anisylacetone	50 per cent.	75 per cent.
Dianisylidiacetone	20 ,,	12 ,,

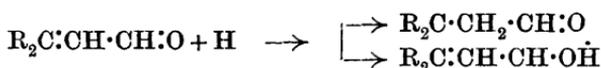
Conclusions.

The electrolytic method of reduction offers many advantages. It is completely under control, and requires very little attention. The reaction mixture is clean and easy to manipulate. It possesses two disadvantages, which greatly restrict its general application. No organic solvent has yet been used that does not readily mix with water. The choice, therefore, is somewhat restricted. The temperature of reduction may not exceed the boiling point of water or of second solvent used. The reduction of very stable substances at higher temperatures, therefore, may not be attempted.

Reduction proceeds in a manner similar to that effected by sodium or sodium amalgam. This resemblance is greatest when an alkaline medium and a cathode composed of lead are employed. The reaction is somewhat different when an acid electrolyte is used. Reduction takes place much more vigorously, and the material of the cathode frequently enters into combination with the intermediate or final products. The latter phenomenon greatly detracts from the utility of lead as the cathode material. Fortunately the reaction is not the same for all metals, and is entirely absent from

copper, tin, amalgamated lead or zinc, and many others. Sheet tin or amalgamated lead are therefore suggested as substitutes for lead, and both come very high in the supertension series.

Unsaturated aldehydes and ketones, containing two reducible groups in a conjugated position, are easier to reduce than compounds with only one reducible group or with two groups widely separated. These facts confirm the now generally accepted view that pairs of double linkings in one molecule mutually augment the properties of the other when brought together into an adjacent position. Each double linking preserves its individuality, however, and reduction may take place at either or both simultaneously. Reduction probably takes place in stages, and commences at the most reactive atom. The starting point of the attack depends on circumstances. The doubly linked carbon pair adds on hydrogen towards the centre of the system. The reverse holds for the carbonyl group, as the oxygen is the most reactive. The reaction thus takes place in one of two directions as represented below:



The two intermediate products act differently according to the conditions. A second atom of hydrogen may be added, two molecular parts may join together, or the metal of the cathode may be attached. The second atom of hydrogen is most readily added in the presence of metallic catalysts. The polymerisation takes place most readily in alkaline solution, and when reduction is undertaken at medium potential. Metallic compounds are formed only in acid solution and with metals like lead, which are slowly attacked by the electrolyte alone, but never with the nobler metals such as copper and mercury.

In conclusion, I wish to express my thanks to the Government Grant Committee for partly defraying the expense of this research