

On the Electrolytic Reduction of Ketones, Part II. The Formation of Hydrocarbons

By

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In the previous communication¹ it was reported that the carbonyl group in an aldehyde can be completely reduced to the methylene group when electrolysed in a moderately concentrated sulphuric acid solution with a current of high density and a cathode of zinc amalgam. It was now found that ketones may also be reduced to the corresponding hydrocarbons in a similar manner.

Of the complete electrolytic reduction of ketones there is only one instance recorded, in which Tafel and his co-workers² electrolysed some aliphatic ketones with a cadmium cathode, and so far as I am aware, no such investigation of aromatic ketones has been made. Hence I attempted to reduce aromatic ketones such as benzoin, benzil, desoxybenzoin, benzophenone, tolylphenyl ketone and others completely to the corresponding hydrocarbons, using the apparatus previously described in the case of complete reduction of aldehydes. As it was necessary to work at a high temperature, the cathode chamber, consisting of a porous cell, was closed with a rubber stopper which was provided with a stirrer, a condenser and a thermometer, and the whole apparatus was placed in a water bath. The gas with the disagreeable smell which is sometimes evolved from the cathode was conducted from the top of condenser into a draught chamber by means of a long delivery tube. The cathode of zinc amalgam was prepared by immersing a circular zinc plate having a diameter of 5.5 cms. and a

1. These Memoirs, **12**, 73 (1929)

2. Tafel: Ber. 42, 3146 (1909); Tafel u. Schepps: Z. Elektrochem., **17**, 972, (1911)

thickness of 1 cm. in a saturated solution of mercuric chloride for an hour, and this was connected to the source of the current with a nickel wire which was tightly enclosed in a glass tube.

When compared with aldehydes, ketones were generally found to be reducible with less resinification in a 70%–85% solution of sulphuric acid at 65°–75°. The presence of an excess of alcohol in the cathode solution should be avoided, otherwise, the yield of hydrocarbon is greatly lowered, as was observed in the case of aldehydes. The hydrocarbon formed by reduction was isolated from the cathode solution by adding a large volume of water to it and then by treating the solution with ether. The ethereal solution was then fractionated after being dehydrated with calcium chloride.

The conditions most favourable for the formation of hydrocarbon were found to be as follows:

Cathode: Zinc amalgam (25 sq. cms.)

Cathode solution: 50–60 c.c. of 70%–85% sulphuric acid
+ 40–50 c.c. of 94% alcohol for every 10 grams of ketone

Temperature: 65°–75°C.

Current strength: 15 amperes.

On passing an electric current 3 or 4 times more than the theoretical quantity necessary for complete reduction, the material yield of hydrocarbon was found to be 60%–90%. As to the relation between the constitution of a ketone and its reducibility, though we are not yet in a position to say anything definite on this point, it may be said that a ketone having a symmetrical structure is reducible with much more ease than that having an assymmetrical form¹. For example, phenyl-para-xylyl ketone is reducible to the corresponding hydrocarbon with a yield of 90%, while the meta- and the ortho-isomers when reduced to hydrocarbons under exactly similar conditions give a yield of 68% and 48% respectively.

It is to be noted here that, when electrolysis is carried out with a concentrated sulphuric acid solution at a high temperature, a gas having a very disagreeable odour is often evolved from the cathode and at the same time the electrode is greatly corroded. In such cases the product of electrolysis partly undergoes decomposition when distilled and produces metallic mercury, showing that some organo-mercury compound is formed together with the hydrocarbon.

1. Law: J. Chem. Soc., 89, 1512 (1909)

From the facts that menthone changes into dimethyl mercury at a mercury cathode¹ and acetone produces tetraisopropyl lead and diisopropyl lead at a lead cathode², Schall and Kirst proposed to infer that the organometallic compound will always be formed as the intermediate product when ketones are reduced to hydrocarbon at a lead, cadmium or mercury cathode. Some facts are, however, contradictory to this assumption. If hydrocarbon is produced through the stage of the organometallic compound it is impossible to explain why high temperature, which favours the formation of the organometallic compound, lowers the yield of hydrocarbon. According to M. Matsui and S. Shimidzu's investigation³, menthone can be reduced to menthane with a yield of about 70% when electrolysed in a sulphuric acid solution containing 20 c.c. of 50% sulphuric acid and 45 c.c. of 94% alcohol at 10°—13° by passing a current of 3 amperes per 28 sq. cms. of mercury cathode, while Schall and Kirst⁴ obtained, as the chief reduction product, dimethyl mercury by working at a higher temperature (70°—75°) with a current of greater density (10 amps./58 sq. cms.).

How the formation of hydrocarbon is related with that of the organometallic compound must be further studied before this problem can be finally solved.

Experiments

1. Reduction of Benzoin

There are no reports in chemical literature on the electrolytic reduction of benzoin to dibenzyl, all the experiments hitherto conducted having been confined to the formation of hydrobenzoin, desoxybenzoin or pinacone. Clemmensen⁵ obtained dibenzyl purely chemically with a yield of 90%, by reducing benzoin with zinc amalgam and hydrochloric acid.

For each experiment 10 grams of benzoin were electrolysed in alcoholic sulphuric acid solutions of the composition described in Table I, and the product was fractionated into three parts. The first

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1. Schall and Kirst: *Z. Elektrochem.*, **29**, 537 (1923)
 2. Tafel: *Ber.*, **44**, 337 (1911)
 3. *These Memoirs*, **4**, 245 (1920)
 4. *loc. cit.*
 5. *Ber.*, **47**, 683 (1914)

fraction boiling at 280° — 295° was obtained as a colourless viscous oil which crystallized on cooling. The main portion of this fraction boiled at 285° — 286° and crystallized to scales melting at 58° , and was afterwards confirmed to be dibenzyl. The second fraction, distilled at 295° — 310° was a brown oil which gradually crystallized into plates. When recrystallized from alcohol, it melted at 124° and showed the properties of stilbene. The third fraction, distilling at 310° — 320° , was separated into stilbene and a substance crystallizing in small plates and melting at 60° . The latter substance was identified as desoxybenzoin by changing it into its oxime and p-nitrophenylhydrazone. The p-nitrophenylhydrazone of desoxybenzoin was obtained as a reddish brown crystal easily soluble in acetone and chloroform and also in hot benzene, toluene and CS_2 , but with difficulty in ligroin and alcohol. It melted at 163° and gave the following results on analysis.

0.1524 gm. substance gave 0.4039 gm. CO_2 + 0.0741 gm. H_2O

$\text{C} = 72.30\%$, $\text{H} = 5.44\%$ (Calc. $\text{C} = 72.48\%$, $\text{H} = 5.17\%$)

The nitrogen content was also determined by Kjeldahl's method after reducing it with zinc dust and salicylic acid. 0.4379 gm. substance produced ammonia which required 30.86 c.c. of 0.1207N—HCl for neutralization.

$\text{N} = 11.91\%$ (Calc. $\text{N} = 12.69\%$)

The relation between the yield of dibenzyl and the composition of the catholyte is shown in the following table:

Table I

No. of exp.	Cathode solution			Current strength in amperes	Time in Hours	Yield %
	Sulphuric acid		Alcohol c.c.			
	%	c.c.				
1	70	50	50	20	1.5	83
2	70	50	50	15	2.0	77
3	70	50	50	10	3.0	76
4	70	50	50	5	6.0	62
5	75	60	50	15	2.0	69
6	70	60	50	15	2.0	80
7	65	60	50	15	2.0	79
8	50	60	50	15	2.0	70
9	30	60	50	15	2.0	44
10	70	30	80	15	2.0	35
11	70	40	70	15	2.0	59
12	70	50	70	15	2.0	80
13	70	50	60	15	2.0	90
14	70	50	50	15	2.0	77

Under the conditions shown in No. 14 in the above table, another series of experiments was conducted with various temperatures, ranging between 60° and 100° , but no significant difference in the amounts of dibenzyl could be observed. The current yield was found to be 67% in an experiment conducted under the conditions shown in No. 3.

2. Reduction of Benzil and Desoxybenzoin

Ten grams of benzil was electrolysed at 70° — 90° under conditions similar to those given in No. 13 in Table I. After 2 hours' electrolysis the yellow oil which separated out on the surface of the catholyte was treated in the same manner as in the case of benzoin and 7.6 grams of dibenzyl were obtained. The yield is thus calculated to amount to 88%.

Desoxybenzoin was also found to be reducible to dibenzyl in just the same manner with a yield of 85%.

3. Reduction of Benzophenone

Ten grams of benzophenone were used for electrolytic reduction and the reduction product was extracted with ether. On fractionating the ethereal extract the fraction distilling at between 260° and 270° was found to consist chiefly of diphenyl-methane. It was purified by repeated distillation and finally obtained as an oily liquid boiling at 264° — 266° and solidifying to long needle crystals with the melting point of 26° when strongly cooled. The relation between the material yield and the electrolytic conditions are shown in Table II.

Table II

No. of exp.	Cathode solution			Tempera- ture °C	Current strength in amperes	Time in hours	Yield %
	sulphuric acid		Alcohol c.c.				
	%	c.c.					
1	75	40	60	65—75	11	2.5	23
2	75	50	60	70—90	15	2.0	65
3	70	50	50	70—90	15	2.0	61
4	70	50	60	70—90	15	2.0	75
5	70	40	60	70—90	15	2.0	34
6	65	50	60	40—50	15	2.0	5

4. Reduction of p-Tolylphenyl Ketone

For reduction, 10 grams of p-tolylphenyl ketone melting at 59° — 60° were employed and the product was purified by fractional distillation. The purified product finally obtained boiled at 277° — 281° and was found to have the specific gravity of 0.9926 at 20° . The presence of more concentrated sulphuric acid was found essential in this case than in the reduction of benzophenone.

The results of these experiments may be tabulated as follows :

Table III

No. of exp.	Cathode solution			Tempera- ture °C	Current strength in amperes	Time in Hours	Yield %
	Sulphuric acid		Alcohol c.c.				
	%	c.c.					
1	70	50	60	70—90	15	2	50
2	80	50	60	70—90	15	2	69
3	85	50	60	70—90	15	2	53

5. Reduction of Xylylphenyl Ketone

Three isomers of xylylphenyl ketone were electrolysed in the same manner as above, 10 grams of them being taken in each experiment. The benzylxylenes obtained by the reduction were found to have the following properties :—

	Sp. gr. (20°)	Boiling point
Benzyl-para-xylene	0.9950	294° — 295°
Benzyl-meta-xylene	0.9951	293° — 298°
Benzyl-ortho-xylene		295° — 298°

Benzyl-ortho-xylene, not previously described in chemical literature crystallizes into plates melting at 33° — 34° and easily dissolves in alcohol, ligroin and benzene.

For confirmation, it was analysed with the following results :

0.2937 gm. substance gave 0.9830 gm. CO_2 + 0.2115 gm. H_2O .

C=91.28%, H=8.06% (Calc. C=91.78%, H=8.22%)

The results of reduction conducted under various conditions are shown below (Table IV) :—

Table IV

No. of exp.	Cathode solution			Tempera- ture °C	Current strength in amperes	Time in Hours	Yield %
	Sulphuric acid		Alcohol c.c.				
	%	c.c.					
para { 1 2 3	80	50	50	75-85	15	2	76
	80	50	40	75-80	15	2	88
	80	50	40	85-90	15	2	71
meta { 4 5	80	50	40	80-85	15	2	68
	85	50	40	65-75	15	2	56
ortho { 6 7	80	50	40	75-80	15	2	37
	75	50	40	75-80	15	2	48

6. Reduction of para-Cymylphenyl Ketone

p-Cymylphenyl ketone was subjected to electrolytic reduction in the same manner as in the previous reductions, and as the reduction product p-cymylphenylmethane was obtained as an oil boiling at 307°-310°. Its specific gravity was determined to be 0.9916 at 20°. The results of the experiments may be tabulated as follows:

Table V

No. of exp.	Cathode solution			Tempera- ture °C	Current strength in amperes	Time in Hours	Yield %
	Sulphuric acid		Alcohol c.c.				
	%	c.c.					
1	80	50	40	75-80	15	2	87
2	85	50	40	70-85	15	2	76
3	85	50	50	75-80	15	2	72

7. Reduction of α -Naphthylphenyl Ketone

The reduction product obtained by the electrolytic reduction of α -naphthylphenyl ketone was distilled and the part distilled out up to 360° was collected. It crystallized on long standing and formed

crystals of a plate form which melted at 58° — 59° . The results of five experiments each conducted with 10 grams of the ketone were as follows :

Table VI

No. of exp.	Cathode solution			Tempera- ture °C	Current strength in amperes	Time in Hours	Yield %
	Sulphuric acid		Alcohol c.c.				
	%	c.c.					
1	80	50	40	75—80	15	2	61
2	85	50	40	75—80	15	2	68
3	85	50	50	65—75	15	2	77
4	85	60	60	70—80	15	2	67
5	90	50	50	65—75	15	2	46

8. Reduction of p-Methoxybenzophenone

Five grams of p-methoxybenzophenone were electrolytically reduced in a manner analogous to that used in the previous experiments. By fractionating the reduction product, p-methoxydiphenylmethane $\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{H}_4\text{OCH}_3$ was isolated as an oil boiling at 305° and having the specific gravity of 1.0496 at 20° . The relation between the yield and the conditions of electrolysis are shown in the following table :

Table VII

No. of exp.	Cathode solution			Tempera- ture °C	Current strength in amperes	Time in Hours	Yield %
	Sulphuric acid		Alcohol c.c.				
	%	c.c.					
1	75	60	20	75—80	15	1	39
2	70	60	20	65—75	15	1	64
3	70	60	20	60—70	15	1	60
4	70	50	30	65—75	15	1	54

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