On the Electrolytic Reduction of Ketones. Part I. Reduction of α, β-Unsaturated Ketones

By

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The carbonyl group in α,β-unsaturated ketones is, in general, reducible to the secondary alcoholic group only with great difficulty, so that, when such ketones are subjected to reduction the corresponding saturated ketones are produced in most cases, but not saturated alcohols[1] which are obtained only very rarely. Sometimes condensation of two molecules is brought about by the addition of hydrogen to the unsaturated bond as was observed by Harries[2] and his co-workers, thus—

$$2C_6H_5 \cdot CH = CH \cdot CO \cdot CH_3 + 2H = \begin{array}{c} C_6H_5 \cdot CH \cdot CH_2 \cdot CO \cdot CH_3 \\ | \\ C_6H_5 \cdot CH \cdot CH_2 \; CO \cdot CH_3 \end{array}$$

$$2C_6H_5 \cdot CH = CH \cdot CO \; C_6H_5 + 2H = \begin{array}{c} C_6H_5 \cdot CH \cdot CH_2 \cdot CO \cdot C_6H_5 \\ | \\ C_6H_5 \cdot CH \cdot CH_2 \cdot CO \cdot C_6H_5 \end{array}$$
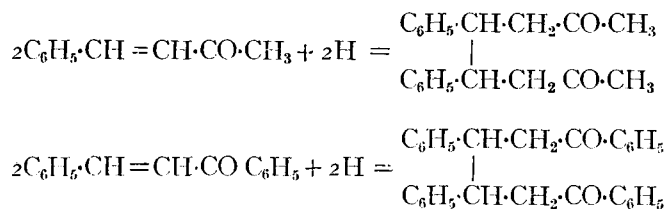
As previously reported[3] I succeeded in reducing cinnamic aldehyde electrochemically to the corresponding saturated alcohol with a yield of more than 70%. An attempt was now made to extend the study to the unsaturated ketones such as benzalacetone and benzalacetophenone, which, however, could not be reduced to the saturated alcohols, the main reduction product being the saturated ketone, as in the case

1. Wallach, Ann., **275**, 111 (1893); Ann., **359**, 283 (1908); Kerp, Ann., **290**, 148 (1896)
2. Ber., **29**, 380 (1896); Ann., **296**, 295 (1897)
3. These Memoirs, **12**, 69 (1928)

of purely chemical reduction.   Engler and Leist[1] once reported that they had obtained phenylbutyl alcohol by reducing an alcoholic solution of benzalacetone with sodium amalgam, but this was disproved by Harries and Eschenbach[2] who could isolate only benzyl acetone and dibenzyl diacetone as the reduction product.

There is a short report on the electrolytic reduction of benzal-acetone by Law[3], who electrolysed in a neutral cathode solution consisting of ethyl acetate, alcohol, water and potassium acetate with a lead or copper cathode and obtained benzyl acetone and dibenzyl diacetone.

When I electrolysed benzalacetone in an alcoholic caustic soda solution with a mercury cathode, a large quantity of a resinous substance was produced together with some benzyl acetone and dibenzyl diacetone, and beside these a new substance hitherto not described in chemical literature was obtained.   It was a yellowish substance boiling at $195°-196°$ under 3 mm. pressure and combining with bromine at ordinary temperatures, and showing the existence of two double bonds when tested by Hanus' method.   As a result of molecular weight determination and elementary analysis it was confirmed to be a pinacone having the composition,

$$C_6H_5·CH = CH·C(OH)·CH_3$$
$$|$$
$$C_6H_5·CH = CH·C(OH)·CH_3$$
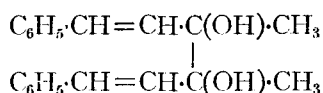
When an alcoholic sodium bicarbonate solution was employed as the the cathode solution, formation of the resinous substance and the pinacone greatly decreased, while the yield of benzyl acetone was increased to more than 90%.   On the other hand the use of a cathode other than mercury, such as lead or copper, was found to favour the formation of dibenzyl diacetone and pinacone.

The reduction of benzalacetophenone was carried out by Schneide-wind[4] and by Harries and Hübner.[5]   The latter authors obtained benzyl acetophenone and dibenzyl diacetophenone by reducing a glacial acetic acid solution with zinc, and diphenyl propyl alcohol and a dihydric

1.   Ber., **6**, 255 (1873)
2.   Ber., **29**, 380 (1896)
3.   J. Chem. Soc., **101**, 1016 (1912)
4.   Ber., **21**, 1325 (1888)
5.   Ann., **298**, 295 (1897)

alcohol of the cyclohexane series on working with an acidified alcoholic
solution and sodium amalgam. The electrolytic reduction of benzal-
acetophenone was first undertaken by Kiyoshi Yamasaki[1] who elec-
trolysed an alcoholic solution acidified with a few drops of sulphuric
acid, using lead or copper as the cathode, and isolated the unsaturated
pinacone,

$$C_6H_5 \cdot CH = CH \cdot C(OH) \cdot C_6H_5$$
$$|$$
$$C_6H_5 \cdot CH = CH \cdot C(OH) \cdot C_6H_5$$
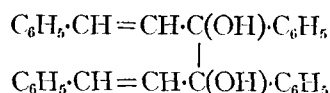
On electrolyzing benzalacetophenone in an alcoholic sodium bicar-
bonate solution to which some ether had been added, at 35°–40°C using
mercury as the cathode, I obtained besides benzyl acetophenone and
dibenzyl diacetophenone, a substance very much resembling the pina-
cone found by Yamasaki, but having the melting point about 10°
higher. All attempts to change this pinacone as well as dibenzyl
diacetophenone to the dihydric alcohol of the cyclohexane series above
mentioned by further reduction having been unsuccessful, I repeated
the reduction of benzalacetophenone according to the Harries and
Hübner method, but could obtain only the unsaturated pinacone melting
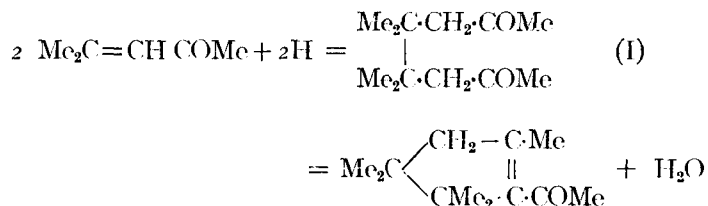at 194°–195°, not the one that the German authors claim to have
isolated.

When the reduction of benzalacetophenone was conducted at a lower
temperature, that is, at about 20°–25° addition of hydrogen to the double
bond chiefly took place, and benzyl acetophenone was produced with a
70%—75% yield.

The influence exerted by ether on the reduction is rather remar-
kable. The reduction conducted with an alcoholic solution containing
no ether yielded, for the most part, a resinous substance and the
reduction-products before mentioned only in very small quantities.
The bad effect of alcohol on the reduction of aldehyde[2] was also
observed in the above reduction, in which the formation of benzyl
acetone and benzyl acetophenone decreased when the concentration of
alcohol was increased.

Inferring from the above confirmed fact that an unsaturated pina-
cone is produced by the reduction of α, β-unsaturated ketone, the view
expressed by Law[3] concerning the formation of desoxymesityl oxide

1. Dissertation not yet published
2. These Memoirs, **11**, 426 (1928); **12**, 71 (1929)
3. J. chem. Soc., **101**, 1016 (1912)

from mesityl oxide may be regarded as very probable. Harries and Hübner[1] assumed the intermediate formation of a diketone (I) which was thought by them to change into desoxymesityl oxide by dehydration, thus—

$$2\ Me_2C=CH\ COMe + 2H\ =\ \begin{array}{c} Me_2C\cdot CH_2\cdot COMe \\ | \\ Me_2C\cdot CH_2\cdot COMe \end{array} \qquad (I)$$

$$=\ Me_2C \begin{array}{c} CH_2-C\cdot Me \\ \diagup \quad \| \\ \diagdown \\ CMe_2\cdot C\cdot COMe \end{array} +\ H_2O$$

The behaviour of desoxymesityl oxide in changing to tetramethyl succinic acid by oxidation and in forming an oxime, $C_{12}H_{21}=NOH,H_2O$ was taken by them to support their view. It was, however, made clear by Law's experiment that the substance which gave tetramethyl succinic acid by oxidation, and changed into an oxime on acting upon hydroxylamine was not desoxymesityl oxide but the intermediate diketone (I). It was further found by him that the reduction of mesityl oxide in an alkaline solution took place in two different ways and gave rise to the unsaturated pinacone of the formula $Me_2C=CH\cdot C(OH)Me$
$$\begin{array}{c} | \\ Me_2C=CH\cdot C(OH)Me \end{array}$$
together with the diketone (I), and this pinacone changed into desoxy-mesityl oxide as the result of the rearrangement. Though in this experiment Law did not succeed in isolating the unsaturated pinacone in the pure state, its existence becomes now quite certain, judging from the result of this work, in which isolation of the unsaturated pinacone was effected.

Experimental

In the following experiments a porous cell was used as the cathode compartment and the cathode solution was always agitated while being electrolysed.

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1. loc. cit.

A. Electrolytic Reduction of Benzalacetone

1. Caustic soda solution.

Cathode solution : 100 c.c. alcohol + 10 c.c. 15% NaOH
          + 10 gms benzalacetone.

Cathode : Mercury (50 sq. cm.).   Temp : 30°–40.°
Anode solution : 10% NaOH.   Current : 2 amp.
Current quantity : 5 amp.–hour.

After electrolysis, the cathode solution, coloured deep red, was diluted with water, and neutralized with dil. H_2SO_4, when a brown resinous substance separated out. This was repeatedly treated with ether, and from the ether extract, the ether was evaporated after dehydration. The oily residue, coloured dark red, was subjected to fractional distillation under reduced pressure, and the following fractions were obtained :—

A part boiling at 100°–110° under 5 mm. pressure   30–35%
„   „   „   „ 210°–220°   „   „   „   25–30%
Residue   35–40%

The first fraction is a colourless resinous oil boiling at 234°–235° under ordinary pressure, and having a density of 0 9892. The result of analysis showed it to be benzyl acetone as follows :

0.2051 gm. substance : 0.6117 gm. CO_2 and 0 1496 gm. H_2O,

C=81.32%(Calc. 81.02%), H=8.16% (Calc. 8.17%).

By treating its alcoholic solution with p-nitrophenyl hydrazine hydrochloride, its nitrophenyl hydrazone was obtained as beautiful orange coloured needles melting at 113°–114°.

The second fraction distilled at 210°–220° under 5 mm. pressure was found to crystallize partly. By treating it with petroleum ether to dissolve oily matter, a white crystalline substance with the melting point of 161° was isolated. This was proved to be dibenzyl diacetone as a result of the following analysis :

0.1316 gm. substance : 0.3904 gm. CO_2 and 0 0593 gm. H_2O,

C=80.91% (Calc. 81.63%), H=7.03% (Calc. 7.48%).

By the action of phenylhydrazine it easily changed into a hydrazone which, when heated, became brown at 170° and melted at 194°.

From the portion soluble in petroleum ether a pale yellowish resinous substance boiling at $194°-195°$ under 3 mm. pressure was isolated. Its density was found to be 1.0842 ($20°$). The results of analysis were as follows :

0.1833 gm. substance : 0,5492 gm. CO_2 and 0.1184 gm. H_2O,

$C = 81.72\%$ (Calc. 81.63%), $H = 7.22\%$ (Calc. 7.48%).

The molecular weight was determined by the ebullioscopic method benzene being used as the solvent, and the values 308.9 and 302.3 were obtained for the calculated value, 294.

In order to find out the number of double bonds, 0.1436 gm. of the substance was dissolved in 10 c.c. of chloroform and treated with 25 c c. of an iodine solution. After this had been allowed to stand for 2 hours, with occasional shaking, 10 c.c. of 10% potassium iodide solution was added, and the whole was titrated with a sodium thiosulphate solution, 1 c.c. of which corresponded to 0.0120 gm. of iodine. The volume of the thiosulphate solution found was 65.3 c.c. as opposed to 85.1 c.c. which was the value found in the blanc test.

$$\text{Iodine value} = \frac{(85 \ 1 - 65.3) \times 0.0120 \times 100}{0.1436} = 165.5$$

$$\text{No. of double bond} = \frac{165.5 \times 294}{126.9 \times 2 \times 100} = 1.92$$

From the results of the above experiments the substance may be concluded to be diphenyl dimethyl dioxyhexadiene of the formula,

$$C_6H_5 \cdot CH = CH \cdot C(OH) \cdot CH_3$$
$$|$$
$$C_6H_5 \cdot CH = CH \cdot C(OH) \cdot CH_3$$
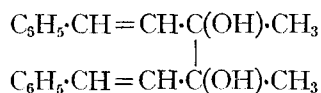
When copper was used as the cathode in place of mercury the yield of benzyl acetone decreased from 35% to 16%, while that of the unsaturated pinacone and of dibenzyl diacetone increased from 18% to 35% and from 7% to 20% respectively.

2. Sodium bicarbonate solution.

In order to ascertain the conditions essential for obtaining benzyl acetone, the influences of cathode material, of temperature, of current density and of concentration of alcohol on the electrolysis of benzal-

acetone were studied, an alcoholic sodium bicarbonate solution being used as the cathode solution. The cathode solution after electrolysis was treated in the same way as the caustic soda solution previously described.

(a) Influence of cathode material

Cathode solution : 50 c.c. alcohol + 10 c.c. water
+ 10 gms. NaHCO₃ + 5 gms. benzalacetone.

Temperature : $20°-25°$; Current density : 2 amp.

Current quantity : 4 amp. hour.

The yield of the reduction-products was as is given in the following table.

Cathode	Benzalacetone %	Pinacone %	Dibenzyldiacetone %
Hg	78	12	3
Pb	66	15	8
Cu	30	37	24

(b) Influence of temperature

Cathode solution : 40 c.c. alcohol + 20 c.c. water + 10 gms.
NaHCO₃ + 5 gms. benzalacetone.

Cathode : Hg.

Other condition were maintained the same as before. The yields were found to be as follows :

Temp.	Benzylacetone %	Pinacone %	Dibenzyldiacetone %
$10°-15°$	72	15	6
$20°-25°$	84	10	2
$35°-40°$	90	–	–
$45°-55°$	84	–	–

(c) Influence of current density

Cathode solution : 30 c.c. alcohol + 30 c.c. water + 10 gms.
NaHCO₃ + 5 gms. benzalacetone.

Temp. : $20°-25°$.

The yield of the reduction products was as follows:

Current density amp./100 sq.cm.	Benzylacetone %	Pinacone %	Dibenzyldiacetone %
2	87	6	–
4	86	8	3
6	90	–	–
8	91	–	–

(d)   Influence of concentration of alcohol

All the conditions were the same as in (a).   The yields of the reduction products were:—

Cathode solution		Benzylacetone %	Pinacone %	Dibenzyldiacetone %
Alcohol (c.c.)	Water (c.c.)			
60	—	72	20	4
50	10	78	12	3
40	20	84	8	2
30	30	86	8	2
20	40	89	–	–

With less alcohol, as the solubility of benzalacetone in the cathode solution becomes insufficient, current effiiciency is greatly lowered.

From the above results, the conditions necessary for obtaining the best yield of benzyl acetone may be summarized as follows:

Cathode: Mercury.   Anode: Platinum or lead.

Cathode solution: 40–50% alcohol containing an excess of $NaHCO_3$.

Anode solution: 5% NaOH solution.   Temp.: $30°–35°$.

Current density: 6–8 amp./100 sq. cm.

It is better to add the benzalacetone to the cathode solution little by little in the course of electrolysis, and to keep the cathode solution always agitated, constantly conducting a current of carbon dioxide into it.

B.   Electrolytic Reduction of Benzalacetophenone

For the electrolysis a cathode solution consisting of 100 c.c. of alcohol and 30 c.c. of ether, in which 10 grams of sodium bicarbonate

and the same amount of benzalacetophenone were dissolved, was taken. This was electrolysed with the cathode of mercury by passing a current of 2.5 amperes. A platinum plate dipped in 10% caustic soda solution was used as the anode. In the course of electrolysis a white precipitate gradually accumulated in the cathode chamber and finally made the cathode solution muddy. After 8 ampere-hours of electricity had been passed, the cathode solution was diluted with water and treated with ether several times so as to dissolve soluble products. By this treatment a white substance was obtained suspended in the ethereal layer.

When collected its amount was found to correspond to 35%–45% of the original substance. After dehydration the ether was next evaporated from the ethereal solution, and a residue consisting of a resinous substance and a white crystalline substance was obtained. It was now treated with alcohol, and from the portion insoluble in alcohol a white crystalline substance melting at $194°$–$195°$ was isolated with a yield of 25%–30%. From the part soluble in alcohol a substance boiling at $210°$–$215°$ under 20 mm. pressure and crystallizing at once was collected with 10%–15% yield, together with a dark brown substance, the quantity of which was found to correspond to 25%–30%.

The substance distilled at $210°$–$215°$ under 20 mm. pressure was purified by crystallizing it from alcohol, and a colourless substance crystallizing in large plates with the melting point of $73°$ was obtained. It was analysed with the following results:

> 0.1778 gm. substance: 0.5560 gm. CO_2 and 0.1055 gm. H_2O,
> C 85.39%, H = 6.60%.
> Calc. for $C_{15}H_{14}O$, C = 85.69%, H = 6.72%.

It could quantitatively be transformed into nitrophenyl hydrazone melting at $137°$–$139°$, when treated with p-nitrophenyl hydrazine hydrochloride. Thus the substance was confirmed to be benzyl acetophenone.

The second substance crystallizing in white fine needles and melting at $194°$–$195°$ was found to dissolve in ether, benzene, toluol and xylol but with difficulty in alcohol. It gave the following results when analysed:

> 0.1885 gm. substance: 0.5933 gm. CO_2 and 0.1081 gm. H_2O,
> C = 85.82%, H = 6.41%.
> Calc. for $C_{30}H_{23}O_2$, C = 86.10%, H = 6.26%.

Its molecular weight was found ebullioscopically to be 413 or 433 by using benzene as the solvent, while the calculated value is 418.

The number of double bonds was also determined by Hanus' method following the manner previously described, and the value 1.92 was obtained. There remains, therefore no doubt that the substance is 1,3,4,6-tetraphenyl-3,4-oxy-hexadiene having the composition,

$$C_6H_5 \cdot CH = CH \cdot C(OH) \cdot C_6H_5$$
$$|$$
$$C_6H_5 \cdot CH = CH \cdot C(OH) \cdot C_6H_5$$
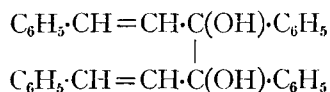
Several experiments were performed to see if this unsaturated pinacone could be transformed into that saturated cyclic glycol which Harries and Hübner claim to have isolated as a substance melting at $210°-211°$. It was electrolytically reduced first in a sodium bicarbonate solution with the cathode of mercury, and then in a glacial acetic acid solution with the cathode of zinc amalgam. sometimes at $20°-25°$ and sometimes at $40°-50°$. Neither of these electrolytic reductions nor a purely chemical reduction conducted with zinc dust having been succesful, Harries and Hübner's method for reducting benzalacetophenone was repeated exactly according to their description. The only reduction product obtained, however, was the unsaturated pinacone melting at $194°-195°$, and no cyclic glycol was found.

The third reduction-product insoluble in ether was also found not to dissolve in other ordinary organic solvents except warm xylol and phenol. It was recrystallized from warm xylol and analysed.

0.1367 gm. substance : 0 4329 gm. CO_2 and 0.0771 gm. H_2O,

C = 86.35%,   H = 6.31%

Calc. for $C_{30}H_{26}O_2$. C = 86.10%, H = 6.26%

The substance is thus proved to be dibenzyl diacetophenone

$$C_6H_5 \cdot CH \cdot CH_2CO \cdot C_6H_5$$
$$|$$
$$C_6H_5 \cdot CH \cdot CH_2CO \cdot C_6H_5$$
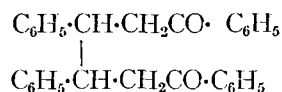
The relation of the yields of the reduction products to the cathode solution and temperature is summarized in the following table :

Cathode solution			Temp.	Benzyl acetophenone %	Unsaturated pinacone %	Dibenzyl diacetophe-none %	Resinous matter %
Alcohol	Ether	Water					
100 c.c.	— c.c.	— c.c.	20°–25°	—	4	2	80
″	—	30	35°–45°	12	35	45	7
80	20	—	50°–55°	20	14	28	18
″	″	30	35°–40°	24	14	20	20
″	″	″	15°–20°	68	8	1	20
70	30	″	″	70	–	–	20

In conclusion, the writer wishes to express his heartiest thanks to Professor M. Matsui for his kind guidance and encouragement throughout this investigation.