ON THE CATALYTIC HYDROGENATION OF THE CARBONYL GROUP IN AROMATIC COMPOUNDS UNDER PRESSURE IN THE PRESENCE OF COPPER. PART II.

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In the previous communication(3) it was published that copper is a suitable catalyst for hydrogenation of carbonyl group in aromatic compounds under pressure in order to get alcohols, and the experiments with diketones were shown. In this paper we describe the experiments with monoketones.

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(3) B. Kubota and T. Hayashi, This journal, **1** (1926), 14.

1. Acetophenone $C_6H_5 \cdot CO \cdot CH_3$. This was treated at 140° (the temperature of the oil bath) under 66 atmospheric pressure (initial) as was described in Part I⁽¹⁾, and a viscous liquid was obtained. It was fractionated under 12 mm. pressure and the following fractions were collected : 80–88°, 88–89° (4%) and 89–92° (very little). The first fraction was found to be unchanged acetophenone forming semicarbazone which melts at 185–186°. The second fraction was warmed with phenyl isocyanate for a few hours on the water bath and allowed to stand over night. The crystalline mass separating out was recrystallised by means of a mixture of alcohol and petroleum ether. It separated out in white crystals melting at 92° and its properties were found to be in good agreement with those of methyl phenyl carbinol of Klages⁽²⁾.

Acetophenone was next treated at 160° under 66 atmospheric pressure. The product consisted of a mixture of a colourless liquid and crystals. The whole mass was fractionated under 15 mm. pressure and the following fractions were collected : 33–34°, 95–96° and residue.

The first fraction was a colourless liquid which distilled at 136–137° under ordinary pressure, and was identified as ethyl benzene. The second fraction proved to be nothing but unchanged acetophenone forming semicarbazone which melts at 185–186°. The residue solidified when cooled and being recrystallised with a mixture of alcohol and petroleum ether, it separated out in needles. It melted with partial sublimation at 123–124° and was, no doubt, dimethyl diphenyl ethane.⁽³⁾

2. Benzophenone. $C_6H_5 \cdot CO \cdot C_6H_5$. This was treated at 120° under 50 atmospheric pressure. The product consisted of colourless crystals with orange-like smell (about 98%) and very small quantities of colourless viscous liquid. The crystals being recrystallised with alcohol were found to melt at 67–67.5° and to possess the properties of diphenyl carbinol, whose benzoic acid ester melting at 82–83° is formed by the fusion with benzoic acid, and whose colour reaction by fuming nitric acid shows blood red and so forth. The liquid product solidified on being cooled with a freezing mixture and melted at 26°, which proved beyond doubt that it was diphenyl methane.

Benzophenone was next treated at 190° under 52 atmospheric pressure. It resulted in a viscous liquid with a good smell (92%) and some crystals. The liquid was subjected to distillation, producing a distillate which boils at 185–212° under 65 mm. pressure and white crystals which remained in the flask. The distillate, crystallising on being cooled in small needles which melt at 26°, proved to be diphenyl methane as described above. The crystals which remained in the frask were recrystallised with alcohol and its pro-

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(1) B. Kubota and T. Hayashi, loc. cit.

(2) Klages and Allendorf, *Ber.*, 31 (1898), 1003.

(3) Engler u. Berthge, *Ber.*. 7 (1874), 1127.

perties were found to be in good agreement with those of tetraphenyl ethane of Zincke.(1)

3. **Camphor $C_{10}H_{16}O$.** Camphor (melting at 176–176.5°, $[\alpha]_D^{15} = +44.51°$) was treated at 120–150° for 12–50 hours under 10–92 atmospheric pressure (initial). The melting points and the compositions calculated from their rotatory power are represented as follows :(2)

Inital pressure of hydrogen.	Duration of the reaction.	Temperature of the oil bath.	Melting point of the product.	$[\alpha]_D$ of the product.	Composition	
					Isoborneol (%)	Borneol (%)
(atm.)	(hour.)					
30	13.4	150	207.5-208.5°	−18.16°	78.8	21.2
10	12	140	204 -206°	−16.53	76.4	23.6
65–92	50	120	204 -205.5°	−12.26	70.9	29.1

The composition was calculated from the following formula given by Beckmann,(3)

$$a = \frac{a_1 m_1 + a_2 m_2}{m_1 + m_2}, \qquad m_1 = \frac{a - a_2}{a_1 - a_2} \times 100,$$

where, a denotes the value of $[\alpha]_D$ of the product,

a_1 ,, ,, ,, ,, $[\alpha]_D$ of L-isoborneol $= -33°$,
a_2 ,, ,, ,, ,, $[\alpha]_D$ of R-borneol $= +37°$,
m_1 denotes the percentage of L-isoborneol,
m_2 ,, ,, ,, ,, R-borneol.

Hulett(4) showed that the effect of the pressure on the melting point of camphor was to be represented by the formula $\frac{dt}{dp} = 0.1290$, up to the pressue of 300 atmospheres. The melting points observed by him between 50 and 175 atmospheres are as follows :

Pressure in atm.	Melting point	Pressure in atm.	Melting point
50	183.7°	125	193.7°
75	187.5	150	197.0
100	190.5	175	200.4

Thus it is clear that the temperature from 120° to 150°, as in the case of our experiments, are not sufficiently high to melt the camphor under the

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(1) Zincke, *Ann.*, 159 (1871), 374.

(2) These results were obtained by the observations of Mr. Ikuo Midzuno.

(3) Beckmann, *J. prakt. Chem.*, 55 (1897), 34.

(4) Hulett, *Z. physik. Chem.* 28 (1899), 657.

pressure of 10–101 atmospheres. This hydrogenation, therefore, was evidently effected in a gas-solid system.

On the other hand, it was shown by Ipatief(1) that the product from hydrogenation of camphor at 200° under 129 atmospheric pressure in the presence of nickel, melted at 210°. In his experiment camphor was subjected to hydrogenation in melted state which differs from the condition of our investigation and the product seems to be consisting of isoborneol for the most part, with a trace ot borneol. (Melting point: borneol=203°, isoborneol=212°).

Whatever method of reduction may have been taken, the borneol obtained from camphor has been found to contain a certain proportion of isoborneol which varies with the condition of reduction as follows :(2)

Method of reduction	Melting point of the product	Amount of isoborneol
Ethyl alcohol+Na	203°–206°	22.4%
Amyl alcohol+Na	203 –204	19.0%
Phenol+Na	203 –204	21.0%

The result obtained by the catalytic hydrogenation in the presence of nickel (by Ipatief), as compared with that in the presence of copper (by us), is as follows :

Method of reduction	Melting point of the product	Amount of isoborneol
(200°, 129 atm.) Hydrogen+nickel	210°	—
(120°, 92 atm.) Hydrogen+copper	204–205.5°	70.9%

It will be found, thus, that copper is a suitable catalyst for the hydrogenation of camphor by means of hydrogen under pressure and the lower the temperature of reduction, the greater is the yield of borneol.

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(1) Ipatief, *J. Russ. Phys. Chem. Soc.*, 38 (1906), 81.

(2) Beckmann, loc. cit.