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

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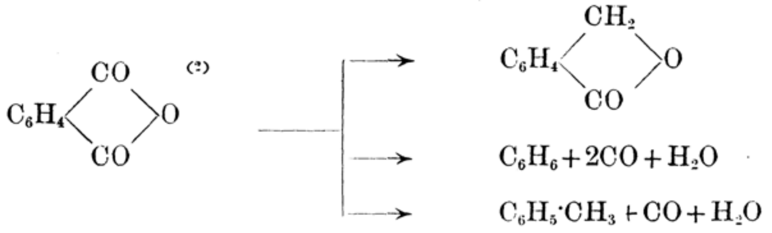
It has been shown by P. Sabatier and his collaborators that the carbonyl group in aromatic compounds undergoes a violent hydrogenation in gaseous system in the presence of copper, giving rise to the formation of hydrocarbons or even to the scission of the molecule, and that it is impossible in general to get any alcohol from aldehyde or ketone by this process of hydrogenation.

$$C_6H_5\cdot CO\cdot C_6H_5^{(1)} \longrightarrow C_6H_5\cdot CH_2\cdot C_6H_5$$

$$C_6H_5\cdot CHO^{(2)} \longrightarrow \begin{cases} C_6H_6 + CO + H_2 \\ C_6H_5\cdot CH_3 + H_2O \end{cases}$$

$$C_6H_5\cdot CO\cdot CH_2\cdot CO\cdot CH_3^{(2)} \longrightarrow C_6H_5\cdot CO\cdot CH_3 + HCO\cdot CH_3$$



On the other hand, Aloy and Brustier(3) have shown that borneol changes into camphor almost perfectly at 300° in the presence of this catalyst. These facts naturally lead one to suppose that, as copper is, under ordinary pressure, evidently a suitable catalyst for dehydrogenation of the carbinol group rather than for hydrogenation of the carbonyl group, the reverse reaction would take place under high pressure;

$$-CH(OH)- \rightleftarrows -CO- + H_2.$$

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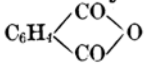
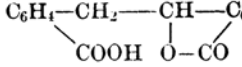
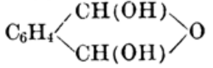
(1) P. Sabatier et Murat, *Compt. rend.*, **158** (1914), 761.

(2) P. Sabatier et B. Kubota, *Compt. rend.*, **172** (1921), 733.

(3) Aloy et Brustier, *Bull. Soc. Chem.*, **9** (1911), 733.

This view has been found to be correct from the following experiments. Diketones (benzil, benzoyl acetone, and phthalic anhydride) and monoketones (acetophenone, benzophenone and camphor) were hydrogenated in an autoclave by means of hydrogen under high pressure in the presence of this catalyst, all producing expected products. It was found, moreover, that two new compounds, methyl-(β-phenyl-β-oxy-ethyl)-ketone $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3$ and dioxyphthalane $C_6H_4[CH(OH)]_2O$, were obtained from benzoyl acetone and phthalic anhydride. The results may be summarized as follows:

	Substance	Temperature of the oil bath	Pressure (atm.)		Product
			initial	max.	
Diketone	Benzil $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$	100°	76	92	Benzoin $C_6H_5{\cdot}CO{\cdot}CH(OH){\cdot}C_6H_5$ Hydrobenzoin and Isohydrobenzoin $C_6H_5{\cdot}CH(OH){\cdot}CH(OH){\cdot}C_6H_5$
		130	64	80	Hydrobenzoin and Isohydrobenzoin
	Benzoyl acetone $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}COCH_3$	83	68	79	Phenyl-(β-oxy-n-propyl)-ketone $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$ Methyl-(β-oxy-β-phenyl)-ketone $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_3$
		105°	57	69	α-Methyl-γ-phenyl-trimethylene glycol $C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3$
	Phthalic anhydride  $C_6H_4\langle(CO)_2\rangle O$	120	67	82	Hydrodiphthalyl lactonic acid  $C_6H_4(COOH){-}CH_2{-}CH(O{-}CO){-}C_6H_4$ Dioxyphthalane  $C_6H_4\langle(CH(OH))_2\rangle O$
Monoketone	Acetophenone $C_6H_5{\cdot}CO{\cdot}CH_3$	140	66	86	Phenyl-methyl carbinol $C_6H_5{\cdot}CH(OH)\,CH_3$
		160	66	96	Phenyl-methyl-methane $C_6H_5{\cdot}CH_2{\cdot}CH_3$
	Benzophenone $C_6H_5{\cdot}CO{\cdot}C_6H_5$	120	50	61	Diphenyl carbinol $C_6H_5{\cdot}CH(OH){\cdot}C_6H_5$ Diphenyl methane $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$
		190	52	67	Diphenyl methane $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$ Tetraphenyl ethane $(C_6H_5)_2{:}CH{\cdot}CH{:}(C_6H_5)_2$
	Camphor $C_{10}H_{16}O$	120–150	10–90	19–101.	Borneol and Isoborneol $C_{10}H_{18}O$

Experiments with diketones are described in this paper, and those with monoketones will be published in the next communication.

Experimental.

The substance to be hydrogenated was mixed intimately in a pyrex glass tube with about half its weight of fine copper of purple colour, which had been prepared from precipitated cupric hydroxide by the reduction with a very slow current of hydrogen at about 180°. It was placed in the autoclave, to which hydrogen under 60–76 atmospheres was introduced and was heated in an oil bath about 18–30 hours. When the reaction was completed, the whole mass in the pyrex glass tube was shaken up with either, and the ethereal solution was filtered from the catalyst. The solution, after being dehydrated over anhydrous sodium sulphate, was distilled to expel ether, and the product remaining in the flask was examined.

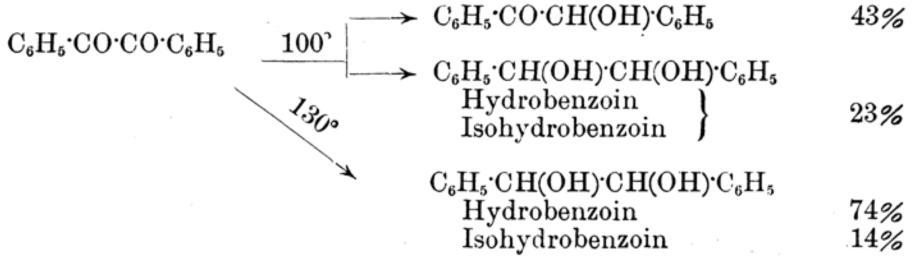
1. Benzil $C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$.

Being treated at 100° (the temperature of the oil bath) under 60 atmospheric pressure (initial) as above mentioned, the mixed product was treated with hot dilute alcohol and was filtered while still hot. Faintly yellow crystals were obtained, which melted at 132° and was identified as benzoin.

To this hot filtrate some hot water was added gradually so long as yellowish oil, which was proved to be unchanged benzil, separated out, and the hot solution was filtered off. When the filtrate was cooled, large crystals separated out. This was found to melt at 134–135° and to possess the characteristic properties of hydrobenzoin, its diacetate being formed by the action of glacial acetic acid on it at 170–180° and so forth.

After filtering the hydrobenzoin, the volume of the filtrate was diminished by evaporation on a water bath, when some crystals of hydrobenzoin again separated out. This was filtered off while still hot and the filtrate was allowed to stand over night. Then some crystals separated out in needles. This substance melted at 94–95° and proved to be isohydrobenzoin.

Similar experiments with benzil was undertaken at about 130° under 64 atmospheric pressure, the products were found to be hydrobenzoin and isohydrobenzoin. Thus the results obtained with benzil may be represented in the following scheme:



2. Benzoyl acetone $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$.

This was treated at 83–87° (the temperature of the oil bath) under 68 atmospheric pressure (initial) as above mentioned. A large quantity of crystalline substance, which proved to be nothing but unchanged benzoyl acetone, and a colourless viscous liquid with a good smell were obtained. The liquid was filtered, fractionated under 12 mm. pressure, and the following fractions were collected: 125–135° (3%), 135–136° (30%), 150–153° (4%).

The first fraction was found to be nearly pure unchanged benzoyl acetone (melting point, 48°) dissolved in the liquid. The second fraction was shaken up with a dilute caustic soda solution so long as it showed any marked ferric chloride reaction, in order to elliminate a trace of benzoyl acetone. Then the liquid was extracted by means of ether. The ethereal solution, on being dehydrated over anhydrous sodium sulphate and evaporated, gave a liquid boiling at 134–136° under 10 mm. pressure, which on analysis proved to be a new oxyketone. (Found: C=73.23; H=7.99. $C_{10}H_{12}O_2$ requires C=73.15; H=7.32 per cent).

The liquid produced an yellow turbidity on the addition of a solution of phenylhydrazine in acetic acid, which precipitated together after a few hours. This was filtered and recrystallised from alcohol. It formed orange crystals melting with partial decomposition at 120–122°. (Found: C=74.80; H=7.01; N=11.35. $C_{16}H_{18}N_2O$ requires C=75.59; H=7.14; N=11.01 per cent).

When it was warmed for some time with acetyl chloride on a water bath, it turned into a colourless viscous liquid with a very good smell.

These facts show that the product is evidently an oxyketone, suggesting as its constitution either of the two following formulae:

$C_6H_5 \cdot CO \cdot CH_2 \cdot CH(OH) \cdot CH_3$ (1), $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO \cdot CH_3$ (2).

By the condensation of acetophenone with acetaldehyde, Staudinger and Kon(1) obtained a viscous liquid boiling at 150–153° under 12 mm. pressure, which proved to be phenyl-(β-oxy-n-propyl)-ketone (1). The properties of the third fraction were found to be in good agreement with those of the oxyketone of Staudinger and Kon.

It is now clear that the second fraction is a new oxyketone represented by the formura (2): $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO \cdot CH_3$.

In the course of their investigation on catalytic hydrogenation of several aliphatic-aromatic carbonyl compounds in presence of palladium, Straus and Grindel(2) have shown that the hydrogenation of those compounds in which the carbonyl group is in the α-position to the benzene ring is carried out more quickly than the other carbonyl compounds. Our result with benzoyl

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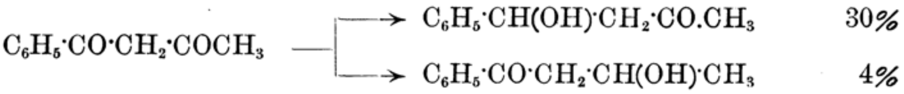
(1) Staudinger and Kon, *Ann.*, 384 (1911), 124.

(2) Straus and Grindel, *Ann.*, 439 (1924), 276.

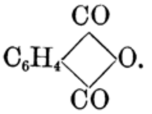
acetone is obviously in complete agreement with that of Straus and Grindel, being represented by the following scheme:



$$C_6H_5\cdot CO\cdot CH_2\cdot COCH_3 \longrightarrow C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO.CH_3 \quad 30\%$$

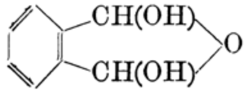
$$C_6H_5\cdot CO\cdot CH_2\cdot COCH_3 \longrightarrow C_6H_5\cdot CO\cdot CH_2\cdot CH(OH)\cdot CH_3 \quad 4\%$$

Benzoyl acetone was next treated at 105° under 57 atmospheric pressure. The product was a liquid which was fractionated under 12 mm. pressure and the following fractions were collected: 135–160° (very little), 162–166° (70%), 167–172° (25%). The properties of the second fraction were found to be in good agreement with those of α-methyl-γ-phenyl trimethylene glycol, $C_6H_5\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH_3$, of E. Bauer.⁽¹⁾

3. Phthalic anhydride 

$$C_6H_4\langle{}^{CO}_{CO}\rangle O.$$

This was treated at 120° under 67 atmospheric pressure (initial) and the result was, that a large quantity of white crystals and some green viscous liquid were obtained. This was drained on a funnel with a perforated plate and the filtrate was shaken up with dilute hydrochloric acid when the green colour of the liquid disappeared. This was washed several times with a dilute sodium carbonate solution, then with water, and extracted with ether. The ethereal solution was dehydrated over anhydrous sodium sulphate and the ether was distilled off, when a colourless liquid was obtained. (Found: C=63.95; H=5.32. $C_8H_8O_3$ requires C=63.15; H=5.31 per cent). Thus it seems to us that this is a dioxyphthalane,



which has not yet been obtained by any other reaction.

On being treated with benzoyl chloride and sodium hydroxide solution, it gave a viscous liquid which smelled fragrant and was ascertained by analysis to be dibenzoyl ester of dioxyphthalane. (Found: C=73.31; H=4.26. $C_{22}H_{16}O_5$ requires C=73.30; H=4.44 per cent).

The crystalline substance above described, on being recrystallised from alcohol, separated out in colourless plates melting at 197–198°. Its properties were found to be in good agreement with those of hydrophthalyl lactonic acid of Wislicenus.⁽²⁾

As it is known that the phthalic acid and its derivatives are apt to change into phthalic anhydride on being oxidised by air when heated, the

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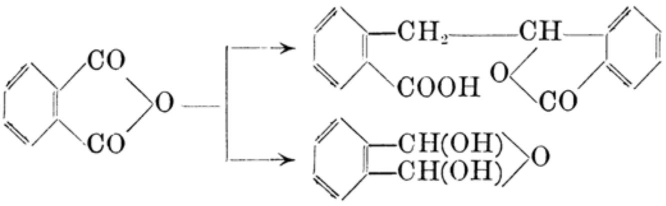
(1) E. Bauer, *Compt. rend.*, **154** (1912), 1093.

(2) Wislicenus, *Ber.*, 17 (1884), 2178.

dioxyphthalane and its benzoyl ester have not been distilled, because they will be decomposed into phthalic anhydride even under 5 mm. pressure.

Now the hydrogenation of phthalic anhydride by this process may be represented by the following scheme:



70% Hydrodiphthalyl lactonic acid of Wislicenus

12% Dioxyphthalane, a new compound.

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