[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE BENZIL REARRANGEMENT. V. CANNIZZARO'S REACTION

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In several recent papers[1] it has been shown that rearrangements of the benzil and pinacol types are essentially questions of intramolecular oxidation and reduction. The present paper deals with Cannizzaro's reaction.

Introduction

As Cannizzaro[2] discovered, benzaldehyde rapidly solidifies when shaken with an excess of a strong solution of sodium hydroxide. Much heat is developed. The reaction mass contains nearly equal molecular equivalents of sodium benzoate and of benzyl alcohol; little or no unchanged benzaldehyde is recovered.

$$2C_6H_5-CHO + NaOH = C_6H_5-COONa + C_6H_5-CH_2OH \qquad (1)$$

This is a typical oxidation-reduction process.

A number of observers have found *that if water is excluded* in this reaction, benzyl benzoate is a primary product. Claisen[3] added sodium methoxide to benzaldehyde, and obtained a mixture of benzyl benzoate and methyl benzoate; and he found that a small amount of sodium benzoxide was capable of converting a large quantity of benzaldehyde directly into benzyl benzoate. Kohn and Tranton[4] heated benzaldehyde with solid sodium hydroxide, in benzene suspension, and were able to isolate some benzyl benzoate from the mixture Tischtschenko[5] obtained esters of benzoic acid when he treated benzaldehyde with aluminum alcoholates.

Action of Aqueous Alkali on Benzaldehyde

Benzyl benzoate is formed, however, even in the presence of water, if precautions are taken to prevent its subsequent hydrolysis. These precautions involve merely avoidance of an excess of alkali, and prevention of any considerable rise in temperature. In the following table are given some of the results obtained.

In each case, 106 g. of benzaldehyde was shaken in a tightly stoppered flask, with sodium hydroxide solution. After a few minutes, when emulsification had taken place, the mixture was stood in cold water for the periods noted. To isolate benzyl benzoate, the mass was covered with ether, and sufficient cold water added, with stirring, until complete solu-

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[1] Lachman, THIS JOURNAL, **44**, 330 (1922); **45**, 1509, 1522, 1529 (1923).

[2] Cannizzaro, *Ann.*, **88**, 129 (1853).

[3] Claisen, *Ber.*, **20**, 646 (1887).

[4] Kohn and Tranton, *J. Chem. Soc.*, **75**, 1155 (1899).

[5] Tischtschenko, *Chem. Centr.*, [II] **77**, 1309, 1552 (1906).

tion occurred. The ether solution was separated, filtered, evaporated and the ether distilled at atmospheric pressure until the vapor temperature reached 220°; the residue was finally distilled at 15 mm. pressure until the temperature of the vapors reached 200°. There was usually a small amount of still higher-boiling residue. From the alkaline solution, benzoic acid was precipitated and weighed. The amount of benzyl alcohol produced, and of unchanged aldehyde recovered, was not estimated. The yields varied irregularly, as must be expected on account of the uncontrolled heating at the start. When 10 *N* alkali is used, the emulsion is very thin, and does not thicken much as reaction proceeds; and the rate is very slow. With a concentration of 14 *N* or over, a very thick emulsion forms rapidly, which sets to a hard cake in a short time, and must be cooled promptly to prevent complete hydrolysis of the ester.

NaOH added Mol. eq.	Time Hours	Benzyl benzoate G.	Benzoic acid G.
NaOH concentration 10 *N*			
0.5	2	..	2
.5	2	1	1
.5	18	9	8
.5	24	3	7
.5	48	8	5
.5	48	6	9
.5	72	7	8
.5	96	5	18
.25	48	5	8
..	..	..	..

NaOH added Mol. eq.	Time Hours	Benzyl benzoate G.	Benzoic acid G.
NaOH concentration 14 *N*			
0.5	4	5	27
.5	48	3	35
.25	48	7	16
.10	48	4	6
NaOH concentration 19 *N*			
.5	24	9	51
.25	24	12	28
.10	18	10	8
.10	24	8	12
.10	72	9	13

The benzyl benzoate obtained above is not entirely pure. 1.40 g., boiled with dil. sodium hydroxide, used up 5.9 cc. of *N* solution, gave 0.72 g. of benzoic acid, melting at 121.5°; ester content, 89%. A number of samples, combined and carefully refractioned at 5 mm., gave considerable dibenzyl ether, boiling at 130–135°, in addition to the main fraction at 150–155°, which was practically pure benzyl benzoate; there was also a small amount of a high-boiling product. The origin of dibenzyl ether is discussed below.

It is interesting to note that in several instances mentioned above, nearly half of the total amount of benzoic acid produced could be isolated in the form of the ester. The failure of the reaction to proceed to completion, especially when 10 *N* alkali was used, is probably entirely a matter of solubility relations, and not of alkali concentration; 106 g. of benzaldehyde was dissolved in 150 cc. of methyl alcohol, and 0.5 equivalent of sodium hydroxide dissolved in 50 cc. of water was added. The alkali was therefore 2.50 *N*, only $^1/_4$ of the lowest concentration used above. The perfectly homogeneous liquid began to warm up almost immediately; it was placed in cold water, and soon solidified. After 24 hours, 46 g. of benzoic acid and 6 g. of benzyl benzoate were obtained.

Dibenzyl Ether

Dibenzyl ether was first obtained by Cannizzaro,[6] upon heating benzyl alcohol with boric anhydride. Later, Lowe[7] prepared the ether by the action of benzyl chloride on sodium benzoxide. A few years ago, Meisenheimer[8] showed that considerable quantities of dibenzyl ether appear when benzyl alcohol is prepared from benzaldehyde, and he traced its formation to the use of sodium bisulfite to remove unchanged aldehyde. Small amounts of sulfurous acid are retained in the benzyl alcohol, and during its distillation catalytically convert the alcohol into its ether.

During the course of the present work, it has been found that alkalies also convert benzyl alcohol into its ether; 50 g. of benzyl alcohol, freshly distilled in a vacuum, was warmed on the water-bath for 4 hours with 25 cc. of 10 N sodium hydroxide; 0.9 g. of dibenzyl ether was obtained. The same quantities, boiled for 2 hours, gave 0.8 g.

In fact, the dehydration of benzyl alcohol may take place without any catalyst at all, other than the glass vessel in which it is heated; 30 g. of freshly rectified benzyl alcohol was heated in a sealed tube to 210–215° (b. p., 207°) for 5 days. No pressure was observed when the tube was opened. Water had visibly separated; on distilling the mixture, the products obtained were 2.0 g. of water, 6.0 g. of unchanged benzyl alcohol, 3.0 g. of dibenzyl ether, and 17 g. of other substances which came from a decomposition of most of the dibenzyl ether that had formed, namely, 6.9 g. of toluene, 6.1 g. of benzaldehyde, 3.8 g. of high-boiling residue.

The heat decomposition of dibenzyl ether, just referred to, was discovered by Cannizzaro. Lowe repeated the observation; and a brief study was published by Oddo.[9] Lowe gives the decomposition temperature as at or above the boiling point, 295–298°. The reaction occurs, however, at a much lower temperature; 30 g., freshly distilled in a vacuum, was heated for 5 days, in a sealed tube, to 210–215°. No gas was formed; the products were 8.5 g. of toluene, 7.5 g. of benzaldehyde, 8 g. of unchanged ether and 5.5 g. of high-boiling residue. No trace of water was found. The main reaction thus corresponds to the equation

$$C_6H_5-CH_2-O-CH_2C_6H_5 = C_6H_5-CH_3 + C_6H_5CHO \qquad (2)$$

The bulk of the high-boiling residue is formed from dibenzyl ether and not by condensation of benzaldehyde; the molecular ratio of toluene and of benzaldehyde isolated is 1:0.8. The high-boiling residue is a complex mixture; the chief component is an oil, boiling constant at 217° (5 mm.).

The pyrolytic decomposition of dibenzyl ether is evidently also a matter of intramolecular oxidation and reduction. The reaction sheds light

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[6] Cannizzaro, *Ann.*, **92**, 113 (1854).

[7] Lowe, *Ann.*, **241**, 374 (1887).

[8] Meisenheimer, *Ber.*, **41**, 1420 (1908).

[9] Oddo, *Gazz. chim. ital.*, **31**, I, 367 (1901).

on some obscure phenomena. O. and W. F. Kamm[10] have recently discussed the appearance of dibenzyl ether during the preparation of benzyl benzoate. They suggest that the addition product of benzyl benzoate and of sodium benzoxide decomposes as follows,

$$C_6H_5-C(ONa)(OCH_2C_6H_5)_2 = C_6H_5-COONa + (C_6H_5-CH_2)_2O \qquad (3)$$

But *benzyl alcohol*, when heated with sodium benzoxide, also yields sodium benzoate and dibenzyl ether; 2 g. of sodium was dissolved in 30 cc. of *benzyl alcohol*, and the mixture heated to 190° for one hour, in a long, open tube. After cooling the reaction mixture and adding water to it, the alkaline liquid gave 1.4 g. of benzoic acid; and the alcohol contained 2.5 g. of dibenzyl ether. As it was possible that benzoic acid owed its production to atmospheric oxygen, the experiment was repeated; the tube was drawn out before the sodium was dissolved, and sealed immediately afterwards. After heating to only 150° for 45 hours, 0.9 g. of benzoic acid, 1.4 g. of dibenzyl ether, and 1.2 cc. of toluene were isolated. No gaseous products were noted.

It is clear that when benzyl alcohol is heated with sodium benzoxide, dibenzyl ether is formed.

$$C_6H_5CH_2OH + C_6H_5CH_2ONa = C_6H_5CH_2-O-CH_2C_6H_5 + NaOH \qquad (4)$$

The ether undergoes metakliny (oxidation-reduction) as in Equation 2, forming toluene and benzaldehyde; and the latter finally goes over into benzoic acid according to the reaction known by Cannizzaro's name (Equation 1).[11]

Perfumers who use benzyl alcohol have trouble in freeing it from dibenzyl ether and above all, from benzaldehyde.[12] The changes described above must go on slowly at ordinary temperatures, and it is more than likely that they are catalyzed by light. Benzyl alcohol distilled at atmospheric pressure will always contain notable traces of both impurities.

The Action of Bromine on Dibenzyl Ether

A measured amount of bromine was slowly dropped into 48 g. of dibenzyl ether. Each addition caused a rapid rise in temperature, and hy-

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[10] O. and W. F. Kamm, "Organic Synthesis," John Wiley and Son, N. Y., **1922**, p. 60.

[11] When a mixture of sodium and amyl alcohol is used for reduction, large quantities of valeric acid appear. In order to see whether the mechanism of this reaction is the same as that just described, 1.8 g. of sodium was dissolved in 20 g. of amyl alcohol, and the solution heated in a sealed tube for 24 hours, the temperature gradually rising to 220°. The tube contained hydrogen at very high pressure. After water had been added, the alcohol layer was distilled. The first drop passed over at 92° and all distilled below 135°. Valeraldehyde boils at 93°, amyl ether at 176°. From the first portion of the distillate, phenylhydrazine formed 1.2 g. of hydrazone, equivalent to 0.6 g. of valeraldehyde. The water layer yielded 2.6 g. of valeric acid. Amyl alcohol does not form its ether under the conditions described, but loses hydrogen directly to give the aldehyde: $C_4H_9CH_2OH = C_4H_9CHO + H_2$.

[12] Compare G. Blanc, *C. A.*, **16**, 3308 (1922).

drogen bromide soon passed off. The mixture, which was dark red, was maintained at from 70–100° by its own reaction heat. No bromine fumes were visible above the liquid until 80 g. had been added. The mixture was then slowly distilled; 72 g. passed over below 230°. This colorless liquid, which fumed strongly, was allowed to stand overnight with an excess of sodium carbonate solution; it was then refluxed for 1 hour, cooled, and separated. The oily layer was distilled, passing over completely between 196° and 202°; it was practically pure benzyl bromide, and weighed 32 g. The sodium carbonate solution, when acidified, gave 36 g. of benzoic acid.

The action of bromine on dibenzyl ether is given by the equation

$$C_6H_5CH_2-O-CH_2C_6H_5 + 2Br_2 = C_6H_5CH_2Br + C_6H_5-CO-Br + 2HBr \qquad (5)$$

The formation of benzoyl bromide was shown in a separate experiment in which the first distillate was directly treated with alcohol; a large amount of ethyl benzoate was formed, but its separation from benzyl bromide, with nearly the same boiling point, proved difficult. The isolated reaction products, in the experiment detailed above, correspond to a recovery of 80%.

The action of bromine on dibenzyl ether is very similar to that of temperature increase; in both cases metakliny occurs. The yields also correspond closely; making allowance for recovered dibenzyl ether, the amount of toluene found above is 87% of that called for by Equation 2.

The Addition of Benzoyl Bromide to Benzaldehyde

In connection with the present investigation, the substance known as bromobenzyl benzoate was examined. This substance is formed by the addition of benzoyl bromide to benzaldehyde.[13] Action takes place spontaneously, with development of a little heat; when distilled, the substance passes over at about 200°, with complete dissociation into its components, which reunite slowly on cooling.

The reaction is considered to take place as follows:

$$C_6H_5-CO-Br \quad + \quad C_6H_5-CHO \quad = \quad C_6H_5CO-O-CHBrC_6H_5 \qquad (6)$$

The present inquiry was directed towards the nature of the linking,—whether the central carbon atoms are tied to oxygen, as shown, or whether perhaps they are directly united. In the latter case, the substance would be related to benzil or benzoin, and most likely have the structure of benzil hydrobromide, $C_6H_5-CO-C(OH)(Br)C_6H_5$.

No such substance could be prepared by melting benzil and passing dry hydrogen bromide over it; no action of any kind took place.

Forty-five g. of crystalline bromobenzyl benzoate was covered with 50 cc. of absolute alcohol, and allowed to stand in a vessel surrounded by cold water until complete solution occurred. Then a slight excess of sodium

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[13] Liebig and Wohler, *Ann.*, 3, 266 (1832). Laurent and Gerhardt, *Jahresber.*, **1850**, 489. Schiff, *Ann.*, **154**, 347 (1870). Claisen, *Ber.*, **14**, 2475 (1881).

carbonate solution was slowly added, and the mixture distilled at low pressure until most of the alcohol passed over. This contained a small amount of ethyl bromide which was not estimated. After extraction with ether and evaporation of the solvent, an oil was obtained which upon distillation gave 15.9 g. of benzaldehyde, and 8.8 g. of ethyl benzoate; no benzil, benzoin, or other high-boiling residue could be noted. From the sodium carbonate solution 11.8 g. of benzoic acid was recovered.

From these results, bromobenzyl benzoate must be regarded as a compound with oxygen linking, as indicated by its name.

The Mechanism of Cannizzaro's Reaction

The data in the present paper afford definite proof that benzyl benzoate is an intermediate in Cannizzaro's reaction. We can hardly assume that this ester is formed from benzyl alcohol and sodium benzoate in the presence of hydroxyl ion. With reference, however, to the two molecules of benzaldehyde from which it is produced

$$C_6H_5CHO + C_6H_5CHO = C_6H_5CO-O-CH_2C_6H_5 \qquad (7)$$

benzyl benzoate represents the *completion* of an oxidation-reduction process. There must be antecedent steps.

It is well known that compounds containing the carbonyl group readily add sodium alkoxide.[14] These addition products are known to show strongly additive properties towards other carbonyl compounds.[15] We may write the following equation, using (OR) as equivalent to OH or to any alkoxide ion:

$$C_6H_5CH(OR)ONa + C_6H_5CHO = C_6H_5CH(OR)-O-CH(ONa)C_6H_5 \qquad (8)$$

This is entirely analogous to the formation of bromobenzyl benzoate, Equation 6.

The addition product assumed in Equation 8 is closely related to dibenzyl ether; it is a derivative of dihydroxy-dibenzyl ether.

$$C_6H_5CH(OH)-O-CH(OH)C_6H_5 \qquad (9)$$

Dihydroxy-dibenzyl ether is a sort of glycol, and must be expected to undergo readily the typical hydroxyl shift.[16] Applying this metaklinic mechanism to the compound assumed in Equation 8, we have

$$\begin{gathered}C_6H_5CH \div O-C(H)(OR)(ONa)C_6H_5 = C_6H_5CH_2-O-C(OR)(ONa)C_6H_5 = \\ C_6H_5CH_2-O-COC_6H_5 + NaOR \qquad (10)\end{gathered}$$

This mechanism, while largely hypothetical and based on reasoning by analogy, seems to be the best available picture of Cannizzaro's reaction, at the present time. It accounts for the formation of mixed esters, as

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[14] The reaction is probably ionic, addition of OH^- or OR^-. The hydroxide addition products are usually too soluble or too reactive to be isolated, but the work of Kohn and Tranton (Ref. 4) shows their existence in the present instance.

[15] Compare Scheibler and Ziegner [*Ber.*, **55B**, 789 (1922)] for a recent and somewhat striking example of this type of reaction.

[16] Lachman, THIS JOURNAL, **44**, 336 (1922).

observed by Claisen and by Tischtschenko. It also shows how a small amount of NaOR can act catalytically, as it does in the Claisen method of preparing benzyl benzoate. While the glycol shift, in general, is catalyzed by acids, aromatic glycols, such as benzopinacol, are also acted upon by alkalies. The separation of the hydroxyl groups is no barrier to the shifting process, for β-glycols, containing the group, $-C(OH)-CH-C(OH-$, also rearrange in typical fashion.

A similar mechanism will account for the behavior of dibenzyl and dibromobenzyl ether (Equations 2 and 5). As no hydroxyl groups are present, rearrangement is brought about by a shift of hydrogen, and a readjustment of electrons.

Conclusion

While it is advisable to postpone a discussion of the details of electron readjustment until further data have been collected, a few general rules may be stated, which seem to apply to the field covered in the present series of papers.

1. Hydroxyl groups attached to two neighboring carbon atoms (α- or β-position) rearrange to give a carbonyl group, with loss of water.
2. A single hydroxyl group, at least in primary alcohols, tends to form a carbonyl group (aldehyde). The behavior of benzyl and of amyl alcohol illustrates two widely different modes of reaching the same end-point.
3. The carbonyl group tends to add hydroxyl or alkoxyl ion, and go over into carboxyl ion.
4. The readjustment of carbonyl to carboxyl necessarily involves the severance of a carbon-carbon bond; this may occur by *rupture*, producing two smaller molecules, or by rearrangement of the carbon chain. Other things being equal, the latter mode seems to be preferred.[17]
5. The preference for rearrangement over rupture applies also to reactions under Rule 1.

The phenomena of condensation, as in the case of the formation of aceto-acetic ester, seem to contradict Rule 3, but the contradiction is more apparent than real. Condensation is an intermediate step; and a continuation of the process, by the same reagents, leads to carboxyl formation.

One cannot but be struck by the almost purposeful behavior of some chemical substances. Who could have predicted the sequence shown in the conversion of benzyl alcohol into benzoic acid: benzyl alcohol, dibenzyl ether, benzaldehyde, Cannizzaro mechanism, benzyl benzoate, benzoic acid? Is there much difference between such a series of events, and what we call "instinct?"

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[17] Compare the behavior of dihydroxytartaric acid; This Journal, **43**, 2091 (1921). This conversion of carbonyl to carboxyl is also discussed, *ibid.*, **45**, 1533 (1923).

Summary

1. When aqueous alkalies act upon benzaldehyde, benzyl benzoate is a primary product.

2. Dihydroxy-dibenzyl ether is indicated as a prior intermediate, and a mechanism for its formation and its conversion into benzyl benzoate by a glycol-like rearrangement is given.

3. In the development of this problem, some properties of benzyl alcohol and of dibenzyl ether are studied.

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[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORIES OF CANADA]

THE ACTION OF CHLORAL ON CELLULOSE

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Hefter[1] by heating a mixture of glucose and anhydrous chloral at 100° obtained two condensation products of chloral with glucose, namely chloralose (m. p., 187°) and parachloralose (m. p., 227°). Petit and Polonowski[2] and Hanriot and Richtet[3] catalyzed the reaction by the addition of a small quantity of hydrochloric acid and obtained the same condensation products. Meunier,[4] using a large quantity of concd. sulfuric acid, carried out the same condensation with chloral hydrate. In addition to the two chloraloses he isolated a dichloralglucose (m. p., 225°) and a chloralglucosan (m. p., 225°). F. H. Reichel[5] treated glucosan and levoglucosan with chloral hydrate and sulfuric acid and obtained two additional dichloralglucoses (m. p., 268°, 85°). From glucosan he obtained parachloralose but no chloralose, whereas from levoglucosan he obtained chloralose but no parachloralose.

The object of the present investigation was to obtain chloral derivatives of cellulose which might be degraded to chloral-substituted glucoses and to compare them with similar derivatives from starch.

No definite products were obtained by the action of chloral or its hydrate on cellulose even in the presence of catalysts such as hydrochloric acid or zinc chloride. By the use of concd. sulfuric acid and chloral hydrate, as described by Meunier, cellulose yielded considerable quantities of chloralglucoses but no chloral-substituted celluloses or cellulose dextrins.

Experimental Part

Fifty g. of surgical cotton was gradually stirred into a mixture of 100 g. of chloral hydrate and 100 cc. of concd. sulfuric acid contained in a beaker cooled in snow. The

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[1] Hefter, *Ber.*, **22**, 1050 (1889).

[2] Petit and Polonowski, *Bull. soc. chim.*, [3] **11**, 125 (1894).

[3] Hanriot and Richtet, *ibid.*, [3] **9**, 947 (1893); [3] **11**, 37, 303 (1894).

[4] Meunier, *Compt. rend.*, **122**, 142 (1896); *Ber.*, (Ref.) **29**, 177 (1896).

[5] Reichel, *Thesis*, University of Geneva, **1921**. Pictet and Reichel, *Helvetica Chim. Acta*, **6**, 621 (1923).