acetic acid, and platinum oxide[7] was used as the catalyst. The substance took up hydrogen readily, and the procedure was finished in about thirty minutes. The following results were obtained:

Substance		Hydrogen absorbed			Hydrogenation ratio
Mg.	Millimoles	Cc.		Millimoles	
19.9	0.0747	3.68	(757 mm., 21°)	0.152	2.03
23.9	.0898	4.41	(756.5 mm., 23°)	.181	2.01

These results are in excellent accordance with the theory, which requires a hydrogenation ratio of 2 for linoleyl alcohol.

The hydrogenation product was isolated by diluting the acetic acid solution with several volumes of distilled water, filtering the precipitate, redissolving it on the filter in a few drops of methanol, and evaporating the solvent. It was a white, crystalline substance which, without further purification, melted at 57.5–58° (reported for octadecanol-1 58.5°).[8]

p-Nitrophenylurethan.—Linoleyl-p-nitrophenylurethan was prepared by means of p-nitrophenyl isocyanate in benzene solution.[9] After several recrystallizations from methanol, it showed a constant melting point of 91–92°. The analysis[10] gave the following results: Calcd. for $C_{25}H_{38}O_4N_2$: C, 69.71; H, 8.90; N, 6.51. Found: C, 68.95, 69.10; H, 8.73, 8.67; N, 6.38, 6.42.

I wish to acknowledge my indebtedness to Professor Herbert M. Evans for the facilities afforded for this work and for his help and advice.

Summary

Linoleyl alcohol, a compound not previously described, has been prepared from methyl linoleate. Some of its properties are given, and its behavior with halogens and catalytically activated hydrogen is described. The alcohol has also been converted into linoleyl-p-nitrophenylurethan.

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[7] V. Voorhees and R. Adams, THIS JOURNAL, **44**, 1397 (1922).

[8] P. A. Levene, C. J. West and J. van der Scheer, *J. Biol. Chem.*, **20**, 521 (1915).

[9] R. L. Shriner and R. F. B. Cox, THIS JOURNAL, **53**, 1601 (1931).

[10] I am obliged to Merck & Co., Inc., Rahway, New Jersey, for this analysis.

BERKELEY, CALIF. RECEIVED NOVEMBER 16, 1937

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

Reductions of Benzil

BY IRWIN A. PEARL AND WILLIAM M. DEHN

Benzil is unique because it yields a large number of reduction products. Without additions of hydrogen to the rings there are fourteen monomolecular reduction products of benzil, namely, *d*- and *l*-benzoin, *cis*- and *trans*-dihydroxystilbene, *cis*- and *trans*-stilbene, *d*-, *l*- and *meso*-hydrobenzoin, *d*- and *l*-phenylbenzylcarbinol, tolane, desoxybenzoin, and dibenzyl. In addition to these there is one split reduction product, toluene, and numerous bimolecular products including well-known compounds such as didesyl, benzoin pinacone and desoxybenzoin pinacone. The number of geometric and stereoisomers of the bimolecular products makes a list too large to recite here. However, only sixteen reduction products of benzil are known, and of these only six have been prepared directly from benzil, namely, benzoin,[1–5] hydrobenzoin,[1,2] isohydrobenzoin,[3] dibenzyl,[1,6] desoxybenzoin[1] and benzoin pinacone.[1] We have prepared six others from benzil, namely, stilbene, isostilbene, phenylbenzylcarbinol, didesyl, isodidesyl, and β-desoxybenzoin pinacone. Also most of these twelve reduction products have been prepared in greatly improved yields.

Because different reducing agents and modifications of conditions used with one reducing agent yield varied products, benzil itself is, perhaps, the most interesting compound for purposes of study of reduction.

Experimental

Preparation of Benzil.—Benzil was prepared from benzoin[7] by oxidation with copper hydroxide in water solution. Clark and Dreger[8] oxidized benzoin to benzil with copper hydroxide in pyridine solution. The disadvantages accompanying the use of pyridine are overcome in the following method.

A concentrated solution of 125 g. of hydrated copper sulfate was stirred mechanically while a 20% solution of 40 g. of sodium hydroxide was added. The mixture was heated to boiling and 40 g. of powdered benzoin was added slowly. The boiling and stirring were continued for

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[1] Beilstein, Fourth Ed., VII, p. 748.

[2] Kubota and Hayashi, *Bull. Chem. Soc.* (*Japan*), **1**, 14 (1926).

[3] Gomberg and Bachmann, THIS JOURNAL, **49**, 2584 (1927).

[4] Buck and Jenkins, *ibid.*, **51**, 2163 (1929).

[5] Bachmann, *ibid.*, **53**, 2758 (1931).

[6] Clemmensen, *Ber.*, **47**, 683 (1914).

[7] Benzoin was prepared by the method of Adams and Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y. (1932), p. 88.

[8] Clark and Dreger, *ibid.*, p. 81,

REDUCTIONS OF BENZIL

No.	Benzil, g.	Reducing agent,[a]	g.	Temp., °C.	Time, hrs.	Product	Yield, %	Crude m. p., °C.	Recryst.[b] m. p., °C.	Identified by method[c]
1[10]	70	KI	47	95	15[d]	Desoxybenzoin[11]	70	55–60	58–60	I
		Red P	10			β-Desoxybenzoin pinacone	12	170	171	IV
		HCl (concd.)	26 cc.							
2	25	Zn amal.[12]	50	15	2–3	Stilbene	85	118–120	124	II
		HCl	100 cc.			Phenylbenzylcarbinol[e]	10	b. p. 160–170 (10 mm.)	66–68	IV
3	20	Zn amal.	20	15	2–3	Benzoin	90	133–135	134–135	III
		HCl	40 cc.							
4	25	Sn amal.[f]	25	25	3–4	Benzoin	96	134–135	134–135	III
		HCl	50							
5	50	Sn amal.	100	75	16	Desoxybenzoin	97	52–60	58–60	I
		HCl	200 cc.							
6	25	Al	8	5	0.5	Benzoin	90	134–135	134–135	III
		HCl	50 cc.			Isodidesyl[g]	5	161	161	IV
7	25	Al amal.	12	25	24	Benzoin	90	134–135	134–135	III
8	25	Al amal.	12	25	2	Benzoin	90	134–135	134–135	III
		HCl	75 cc.							
9	22	Zn	32	100	2	Didesyl	30	245–250	248–250	IV
		NaOH	40			Benzoin pinacone	10	208	208	IV
						Isodidesyl	6	160	161	IV
10	10	Zn	30	95	3	Desoxybenzoin	64	56–58	58–60	I
		NH_4OH (concd.)	200 cc.							
11	25	Mg amal.	15	5	3	Benzoin	90	134–135	134–135	III
		HCl	75 cc.							
12	25	Zn	60	25	4	Benzoin	65	118–124	134–135	III
		NH_4Cl								
13	25	Zn	60	25	4	Benzoin	99	134–135	134–135	III
		NH_4Cl	25							
14	25	Zn	50	100	2	Benzoin pinacone	10	208	208	IV
		H_3PO_4 (85%)	150							

[a] In all cases alcohol was used as the solvent except in the following experiments: (1) no solvent; (7) 90% alcohol; (9), (10), (13) water. [b] Alcohol was used as the recrystallizing solvent in all experiments. [c] Identification methods: I = semicarbazone, II = dibromide, III = acetate, IV = mixed melting point. [d] The yield of pinacone increased with the time of heating, thus indicating that desoxybenzoin is an intermediate product in the formation of β-desoxybenzoin pinacone from benzil. [e] Phenylbenzylcarbinol was converted to stilbene by short boiling with acetic anhydride, distilling and recrystallizing from alcohol. [f] The tin amalgam was prepared by allowing a mixture of 100 g. of powdered tin (20-mesh), 15 g. of mercuric chloride, and 100 cc. of water to stand in a flask with occasional shaking until the tin acquired a shiny coating of mercury. The solution was decanted and the amalgam was washed with water. [g] Obtained by extracting with ether the mixture obtained when the alcoholic filtrate was poured into water.

forty-five minutes while keeping the volume of the mixture constant by the addition of water. The reaction mixture was cooled and filtered. The precipitate was boiled with 200 cc. of alcohol and filtered hot. On cooling, the filtrate yielded 35–37 g. of needles melting at 94–95°. A second extraction yielded an additional 3 or 4 g. or a total of 90–95% of pure benzil. This benzil gave no test with Fehling's solution.

If 85 g. of sodium hydroxide was substituted for the 40 g. given here, a transformation of benzoin to benzilic acid was obtained. After heating for forty-five minutes, the hot mixture was filtered and the precipitate was extracted with a little hot water. The combined filtrates were then cooled and acidified with dilute hydrochloric acid. The benzilic acid which separated weighed 40 g. or 93% and melted at 149–150°.[9]

Reduction of Benzil with Zinc Amalgam and Phosphoric Acid.—To a mixture of 50 g. of benzil, 100 g. of zinc amalgam, and 350 cc. of alcohol was added with stirring 175 cc. of 85% phosphoric acid while keeping the temperature below 15°. After the addition of the acid (one to one and one-half hours), the mixture was poured into an excess of cold water, stirred for a few minutes and filtered. The precipitate was extracted with 200 cc. of hot alcohol to remove the zinc and zinc phosphate. On cooling, the filtrate yielded 26 g. or 55% of iridescent plates of stilbene melting at 124°. Its dibromide melted at 238°.

The alcoholic filtrate was evaporated to a heavy oil which yielded 17 g. or 35% of isostilbene boiling at 138–145° at 20 mm. Its dibromide was prepared in chloroform and melted at 238°.

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(9) Benzilic acid has been prepared from benzoin by oxidation with sodium bromate and sodium hydroxide (Ballard and Dehn, *ibid.*, p. 82). The method described above is superior to the older method.

(10) This is essentially the method used by Ballard and Dehn, THIS JOURNAL, **54**, 3969 (1932), for the reduction of benzoin.

(11) Japp and Klingmann[1] reported the preparation of desoxybenzoin by heating benzil with concentrated hydriodic acid.

(12) Clemmensen[6] obtained dibenzyl from benzil by boiling with zinc amalgam and hydrochloric acid.

Reduction of Benzil with Aluminum Amalgam and Aqueous Ammonium Hydroxide.—The aluminum amalgam was prepared by adding small pieces of aluminum foil to a dilute solution of mercuric chloride. A vigorous reaction took place and after standing a few minutes, the amalgam was poured upon a Büchner funnel and well washed with water and then with alcohol. This amalgam must be used immediately because of its great reactivity.

Twenty grams of this aluminum amalgam was covered with 300 cc. of alcohol and then 25 g. of benzil in a mixture of 30 cc. of concentrated ammonium hydroxide and 50 cc. of water was added. Stirring caused the mixture to become warm. Stirring was continued for two hours and the mixture was allowed to stand till the next day. The yellow color of benzil disappeared, and a thick gray colored precipitate separated. The reaction mixture was poured into a large excess of dilute hydrochloric acid to dissolve the precipitated aluminum hydroxide. The precipitate was filtered and extracted with boiling alcohol. On cooling, 15 g. or 60% of crude hydrobenzoin melting at 128–130° was obtained. Recrystallization from alcohol gave iridescent plates melting at 135°. The mixed melting point with pure hydrobenzoin was 135°.

In an analogous manner benzil was subjected to the action of a number of reducing agents under various conditions. The conditions and data of these experiments are listed in Table I.

Whereas most of these reducing agents give high yields of benzoin, such reductions are only of theoretical interest because benzil itself is prepared from benzoin. However, the other reductions are valuable for the preparation of certain of the other reduction products of benzil.

Attempted Reductions of Benzil.—Whereas reaction of benzil with zinc and sodium hydroxide in water solution yielded didesyl, the reaction with zinc and sodium hydroxide in alcoholic solution gave a 90% yield of benzilic acid melting at 150°.

No reactions on benzil were obtained with aluminum and sodium hydroxide in alcoholic solution or with zinc amalgam and sodium hydroxide in water solution or with magnesium amalgam in water solution.

Summary

The effects of a number of various reducing agents and reducing conditions on benzil have been studied. Six new reduction products of benzil, namely, stilbene, phenylbenzylcarbinol, isostilbene, didesyl, isodidesyl, and β-desoxybenzoin pinacone have been obtained directly from benzil.

SEATTLE, WASHINGTON RECEIVED SEPTEMBER 21, 1937

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

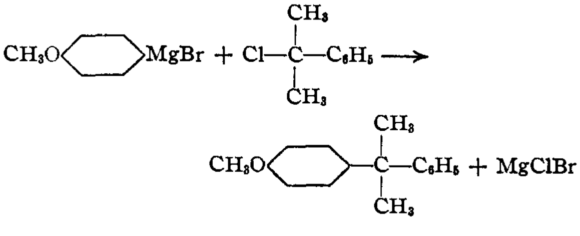
The Condensation of Some Tertiary Aryl Substituted Carbinols with Phenol in the Presence of Aluminum Chloride

BY LLEWELLYN H. WELSH WITH NATHAN L. DRAKE

Various types of carbinols have been condensed with aromatic compounds in the presence of aluminum chloride. Primary,[1] secondary[2] and tertiary[3,4] aliphatic alcohols, and primary and secondary aryl substituted carbinols[5] have been found to react with benzene under suitable conditions to yield alkyl- and arylalkyl-benzenes. These same types of alcohols[4,6,7,8], also have been condensed with phenol to form, usually, para-substituted phenols.

The purpose of the present work was to effect the condensation of some tertiary aryl substituted carbinols with phenol in the presence of aluminum chloride, and to obtain additional evidence concerning the mechanism of reactions between alcohols and aromatic compounds. Phenol rather than an aromatic hydrocarbon was selected as a reactant because greater ease of reaction and more efficient separation of products from reaction mixtures were anticipated.

Dimethylphenylcarbinol reacted with phenol to give 68–72% yields of p-(α,α-dimethylbenzyl)-phenol. That the dimethylbenzyl group entered para to the hydroxyl was proved by the following synthesis



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(1) Tzukervanik and Vikhrova, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 632 (1937); *C. A.*, **31**, 5779 (1937).

(2) Tzukervanik and Tokareva, *ibid.*. **5**, 764 (1935); *C. A.*, **30**, 442 (1936).

(3) Tzukervanik, *ibid.*, **5**, 117–120 (1935); *C. A.*, **29**, 4746 (1935).

(4) Huston and Hsieh, THIS JOURNAL, **58**, 439 (1936).

(5) Huston and Friedemann, *ibid.*, **38**, 2527 (1916); *ibid.*, **40**, 785 (1918).

(6) Tzukervanik and Nazarova, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 623 (1937); *C. A.*, **31**, 5778 (1937).

(7) Huston, THIS JOURNAL, **46**, 2775 (1924).

(8) Huston, Lewis and Grotemut, *ibid.*, **49**, 1365 (1927).