for three or four days at 5°. The colorless crystals are filtered off, washed with two 50-cc. portions of glacial acetic acid, then with two 50-cc. portions absolute alcohol, air-dried for a day and then for eight hours in an 80° evacuated oven; yield, 325 g. (70%); $[\alpha]^{20}_{D}$ +14.8 (constant) in water compared with +14.6 found by Hudson and Yanovsky.[14] About half of the mannose in the mother liquor may be precipitated as a sirup by ether and reconverted into methyl mannoside, but in general this is not profitable.

Summary

The preparation of crystalline *d*-mannose from the hydrolysis of vegetable ivory by the intermediate preparation of its phenylhydrazone and its reconversion to mannose with benzaldehyde has been superseded in recent years by the direct crystallization of the sugar from the hydrolyzed material through the use of glacial acetic acid as the solvent of crystallization. This method, while often successful, is not always dependable, probably because of variations in the quality of the vegetable ivory. In a previous paper directions were given for preparing pure crystalline α-methyl-*d*-mannoside in good and regular yield (45%) from vegetable ivory. It is now shown that this pure mannoside may be used as a source for the preparation of crystalline mannose in a yield of 70%, corresponding to an over-all yield of about 30% of pure crystalline sugar from vegetable ivory. It is believed that this method is the most suitable at the present time for preparing pure mannose.

WASHINGTON, D. C. RECEIVED JANUARY 6, 1934

---

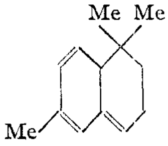
[14] Hudson and Yanovsky, THIS JOURNAL, **39**, 1022 (1917).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

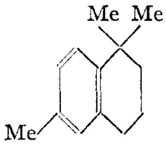
The Synthesis of Condensed Polynuclear Hydrocarbons by the Cyclodehydration of Aromatic Alcohols. II.[1] The Synthesis of Ionenes[2]

BY MARSTON T. BOGERT, DAVID DAVIDSON[3] AND P. MAX APPELBAUM

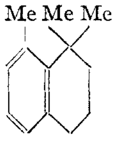
In a recent article, Bogert and Fourman[4] submitted evidence that the hydrocarbon ionene, obtained by the dehydration of either alpha- or beta-ionone, does not possess the structure (I) originally assigned to it by its discoverers, Tiemann and Krüger,[5,6] but is probably the 1,1,6-trimethyltetralin (II), as suggested in 1896 by Barbier and Bouveault.[7]



I



II

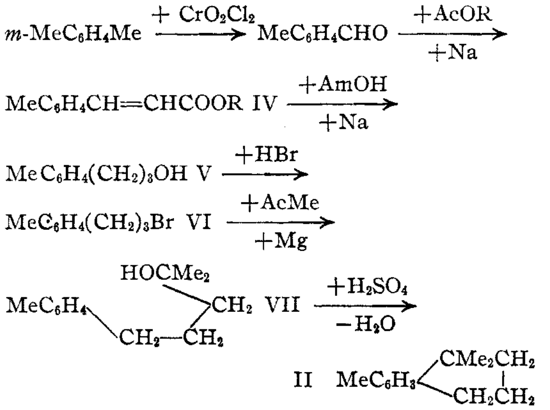


III

This formula (II), deduced experimentally by Bogert and Fourman, has now been established by the synthesis of ionene from *m*-xylene.

As reported in our preliminary announcements in *Science*,[8] the steps in this synthesis were the following:

SYNTHESIS OF IONENE



$$m\text{-MeC}_6\text{H}_4\text{Me} \xrightarrow{+\text{CrO}_2\text{Cl}_2} \text{MeC}_6\text{H}_4\text{CHO} \xrightarrow[+\text{Na}]{+\text{AcOR}}$$

$$\text{MeC}_6\text{H}_4\text{CH{=}CHCOOR IV} \xrightarrow[+\text{Na}]{+\text{AmOH}}$$

$$\text{MeC}_6\text{H}_4(\text{CH}_2)_3\text{OH V} \xrightarrow{+\text{HBr}}$$

$$\text{MeC}_6\text{H}_4(\text{CH}_2)_3\text{Br VI} \xrightarrow[+\text{Mg}]{+\text{AcMe}}$$

$$\text{MeC}_6\text{H}_4\left\langle\begin{matrix}\text{HOCMe}_2 \\ \text{CH}_2\text{—CH}_2\end{matrix}\right\rangle\text{CH}_2 \text{ VII} \xrightarrow[-\text{H}_2\text{O}]{+\text{H}_2\text{SO}_4}$$

$$\text{II MeC}_6\text{H}_3\left\langle\begin{matrix}\text{CMe}_2\text{CH}_2 \\ | \\ \text{CH}_2\text{CH}_2\end{matrix}\right.$$

The final step (cyclodehydration) in this series was the critical one, for it was obvious that the side chain might attach itself to the tolyl nucleus either para or ortho to the methyl group, giving in the former case ionene and in the latter the isomeric 1,1,8-trimethyltetralin (III). When the experiment was carried out, the product proved to be identical with ionene in its physical and chemical properties, and there was no evidence

---

[1] I. THIS JOURNAL, **56**, 185 (1934).

[2] Presented in abstract before the Division of Organic Chemistry, at the Washington Meeting of the American Chemical Society, March 29, 1933.

[3] Research Assistant, Department of Chemistry, Columbia University.

[4] Bogert and Fourman, THIS JOURNAL, **55**, 4670 (1933).

[5] Tiemann and Krüger, (a) *Ber.*, **26**, 2675, (b) **26**, 2693 (1893); (c) **31**, 808 (1898).

[6] Tiemann (a) British Patent 8736 (May 1, 1893); (b) 17,539 (Sept. 18, 1893); (c) *Ber.*, **31**, 873 (1898).

[7] Barbier and Bouveault, *Bull. soc. chim.*, [3] **15**, 1008 (1896).

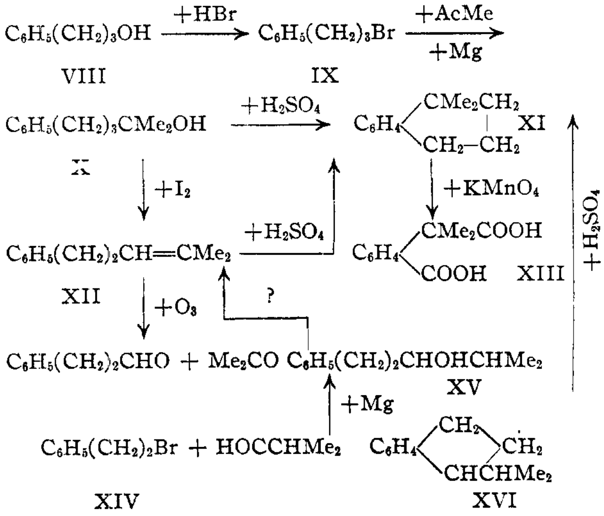
[8] Bogert, (a) *Science*, [N. S.] **76**, 475 (1932); (b) **77**, 197 (1933).

of the presence of any appreciable quantity of the isomer (III).

Inasmuch as such a ring closure (cyclodehydration) might occur either (a) by the direct elimination of the OH of the tertiary alcohol (VII) with a hydrogen of the tolyl nucleus, in the form of water; or (b) by the loss of a molecule of water from the side chain, with production of an olefin, which could then rearrange by cyclization to the isomeric tetralin derivative, it seemed desirable to study the mechanism of this reaction somewhat more in detail. We were led to this decision not solely by our interest in ionene, but also because we have had under way for some time in our laboratories many other cyclodehydrations of similar type as intermediate steps in the synthesis of various polynuclear aromatic hydrocarbons.

In our attack upon this problem, we studied the simple 2-methyl-5-phenylpentanol-2 (X) and 2-methyl-5-phenylpentanol-3 (XV). The lines followed are here summarized schematically.

SYNTHESIS OF 1,1-DIMETHYLTETRALIN



It is well known that tertiary alcohols are easily dehydrated to olefins, and that these olefins in turn may isomerize or polymerize. Among the olefinic terpenes and related compounds, this isomerization frequently takes the form of a cyclization. The reagents usually employed to accomplish this have been sulfuric acid, phosphorus pentoxide, formic acid, acetic anhydride and the like. The formation of geraniolene and cyclogeraniolene from the corresponding alcohol[9] of methyl geranic esters and their cyclization,[10] the dehydration of nerolidol to farnesene with subsequent cyclization to bisabolene,[11] the conversion of pseudoionones into ionones,[5a] of citronellal into isopulegol,[12] are familiar examples of the readiness with which this cyclization of olefinic compounds occurs. Even alkali metals have recently been utilized[13] for this purpose, in the case of aryl olefins.

Referring to the chart, it will be noted that the action of sulfuric acid upon the tertiary alcohol (X) resulted in the production of the 1,1-dimethyltetralin (XI), whose constitution was proved by its oxidation to the α,α'-dimethylhomophthalic acid (XIII). When this same tertiary alcohol (X) was distilled with a small quantity of iodine, there resulted the olefin (XII), whose structure was established by its ozonolysis to hydrocinnamaldehyde and acetone. Heated with sulfuric acid, this olefin (XII) was easily cyclized to the 1,1-dimethyltetralin (XI). It seems probable, therefore that this olefin is an intermediate product in the conversion of the alcohol (X) into the tetralin (XI) by the action of sulfuric acid. In further support of this assumption, the secondary alcohol (XV) likewise yielded the same tetralin (XI) when heated with sulfuric acid, presumably through formation of the same intermediate olefin (XII), although this was not proven. It is obvious that if the OH of the alcohol had condensed with an H of the benzene nucleus, the product should have been the indane (XVI) and not the tetralin (XI).

In the cyclodehydrations described in this paper, we were fortunate in not encountering any appreciable polymerization of the intermediate olefins.

Experimental

The melting points recorded in the following pages were read with a thermometer which was standardized against a partial immersion thermometer certified by U. S. Bureau of Standards. Distillations under reduced pressures were generally conducted with a barostat which kept the pressure constant ±1 mm. Densities were determined with a pycnometer and the usual corrections were applied. Refractive indices were read with a dipping refractometer.

---

[9] (a) Tiemann and Semmler, *Ber.*, **26**, 2724 (1893); (b) **33**, 3711 (1900); (c) Grignard, Thèse de Doctorat, 1901, p. 81; (d) Simonsen, "The Terpenes," University Press, Cambridge, 1931, Vol. I, p. 5; (e) Wallach and Scheunert, *Ann.*, **324**, 99 (1902); (f) Harries and Weil, *Ber.*, **37**, 845 (1904).

[10] Tiffeneau, *Compt. rend.*, **146**, 1153 (1908).

[11] (a) Ruzicka, *Helv. Chim. Acta*, **6**, 483 (1923); (b) Ruzicka and Capato, *ibid.*, **8**, 259 (1925).

[12] Bogert and Hasselström, THIS JOURNAL, **52**, 4093 (1930).

[13] (a) Schlenk and Bergmann, *Ann.*, **463**, 51 (1928); (b) **479**, 65 (1930); (c) Bergmann and Weiss, *ibid.*, **480**, 51 (1930).

Ionene

***m*-Tolualdehyde.**—Carefully purified[14] *m*-xylene (b. p. 138–139°) was oxidized by chromyl chloride (Étard reaction), as described by Bornemann.[15] The yield from four 50 g. lots was 106 g., or 53%, and the product boiled at 94–96° at 23 mm., and 198–199° at 762 mm. Bornemann recorded the b. p. as 199°, without noting the pressure.

Ethyl *m*-methylcinnamate (IV), prepared from the *m*-tolualdehyde by the Claisen condensation,[16] in a yield of 70%, was a colorless liquid, b. p. 128° at 9 mm. and 146–150° at 23 mm. Its agreeable odor recalled that of the unmethylated cinnamic ester. It was easily hydrolyzed to *m*-methylcinnamic acid, m. p. 111.5–112°. Miller and Rhode[17] reported the m. p. of this acid as 111.5°.

3-(*m*-Tolyl)-propanol-1 (*m*-Tolylpropyl Alcohol) (V).—A Bouveault–Blanc reduction[18] of 116 g. of the above ester in commercial amyl alcohol fractioned over calcium oxide, by the action of sodium, gave 62 g., or a 68% yield, of the desired alcohol (V), as a colorless liquid, whose odor faintly recalled that of benzyl alcohol; b. p. 108° at 4 mm., 124° at 10 mm., 147° at 20 mm.; d_4^{25} 0.9776; n_D^{25} 1.52004; M_D obs. 46.79, calcd. 46.30.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.94; H, 9.40. Found: C, 79.41; H, 9.61.

Phenylurethan, m. p. 52–53°.

Anal. Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: N, 5.49.

3-(*m*-Tolyl)-1-bromopropane (*m*-Tolylpropyl Bromide) (VI).—When 58 g. of *m*-tolylpropyl alcohol (V) was treated with hydrobromic acid (48%), in the presence of sulfuric acid,[19] there was obtained 55 g., or a yield of 67% of the bromide (VI). It was a colorless liquid, of characteristic odor; b. p. 104° at 4 mm., and 140–145° at 20 mm.

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.33; H, 6.15. Found: C, 55.98; H, 6.40.

2-Methyl-5-(*m*-tolyl)-pentanol-2 (VII).—A Grignard condensation of 50 g. of the above bromide (VI) with acetone gave 20 g., or 46%, of this tertiary alcohol (VII) as a colorless liquid, of rose-type odor; b. p. 128–132° at 5 mm.; d_4^{25} 0.9493; n_D^{25} 1.50818; M_D obs. 60.36, calcd. 60.16.

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.18; H, 10.49. Found: C, 80.58; H, 10.44.

Phenylurethan, m. p. 97–98°.

Anal. Calcd. for $C_{20}H_{25}O_2N$: N, 4.50. Found: 4.61.

Ionene (1,1,6-Trimethyltetralin, or 1,1,6-Trimethyl-1,2,3,4-tetrahydronaphthalene) (II).—When 10 g. of the tertiary alcohol (VII), kept cold in ice water, was treated dropwise with 18.5 g. (10 cc.) of cold concentrated sulfuric acid, an emulsion formed which gradually separated into two layers. The upper layer was removed. The lower sulfuric acid layer was poured into 25 g. of chopped ice, the mixture extracted with ether and the ether extract added to the reserved upper layer. The resulting ether solution was neutralized with a 10% sodium carbonate solution, dried over anhydrous sodium sulfate and the ether distilled off. The residual liquid was distilled twice over sodium under diminished pressure; yield, 7 g., or 77%.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.58; H, 10.42. Found: C, 89.40; H, 10.50.

In the following table, the properties of this product (A) are compared with those of an ionene (B) prepared by dehydration of α-ionone according to the method of Bogert and Fourman.[4]

IONENE

	Ionene A	Ionene B
B. p., °C.	88–91 at 4 mm.	108–112 at 10 mm.
d_4^{25}	0.9320	0.9299
n_D^{25}	1.52167	1.52163
M_D (calcd. 56.43)	56.82	57.08
E_M	0.39	0.65
Dinitro deriv., m. p., °C.	102	102 (mixed m. p. 101.5)
Sulfonamide, m. p., °C.	158–159	158–159 (mixed m. p. 157.5–158.5)

1,1-Dimethyltetralin

3-Phenyl-1-bromopropane (phenpropyl bromide) (IX) was obtained in a yield of 69% (274 g.) when 272 g. of phenpropyl alcohol was treated with hydrobromic acid (48%), in the presence of sulfuric acid. It formed a colorless liquid, of pungent odor, b. p. 100–102° at 4 mm. and 110–113° at 11 mm.; d_4^{25} 1.3106; n_D^{25} 1.54396; M_D obs. 47.93, calcd. 47.93. Rupe and Bürgin,[20] who prepared it by the action of phosphorus tribromide upon the alcohol, found a b. p. of 109° at 11 mm.

2-Methyl-5-phenylpentanol-2 (X).—By the Grignard reaction, a 51% yield (90.5 g.) of this tertiary alcohol was secured from 199 g. of phenpropyl bromide and the calculated amount of acetone. It was a colorless liquid, of rose-type odor; b. p. 120° at 7 mm., 130° at 10 mm.; d_4^{25} 0.9556; n_D^{25} 1.50681; M_D obs. 55.46, calcd. 55.54.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.51; H, 10.16.

Phenylurethan, m. p. 101.5–102.5°.

Anal. Calcd. for $C_{19}H_{23}O_2N$: N, 4.71. Found: 4.80.

2-Methyl-5-phenylpentene-2 (XII).—When 35.6 g. of the tertiary alcohol (X) was distilled in the presence of a small crystal of iodine, 26.9 g. of yellowish liquid was collected at 215–225°. This was unsaturated toward bromine in carbon tetrachloride or toward aqueous potassium permanganate solution. Redistilled under diminished pressure, 22 g. (69%) of a colorless fraction was collected, b. p. 108–112° at 25 mm.

A sample of this titrated against a cold carbon tetrachloride solution of bromine, showed an olefin content of 85%. This was regarded as sufficiently pure for our purposes, in view of the identification described below and that this olefin was proved to be an intermediate in the cyclodehydration of the alcohol to the tetralin. Oxidation of

---

[14] Clarke and Taylor, THIS JOURNAL, **45**, 831 (1923).

[15] Bornemann, *Ber.*, **17**, 1464 (1884). See also Law and Perkin, *J. Chem. Soc.*, **91**, 258 (1907).

[16] Marvel and King, "Organic Syntheses," Coll. Vol. I, p. 246, 1932, John Wiley & Sons, Inc., New York.

[17] Miller and Rhode, *Ber.*, **23**, 1899 (1890).

[18] Ford and Marvel, "Organic Syntheses," Vol. X, p. 62, 1930, John Wiley & Sons, Inc., New York.

[19] Kamm and Marvel, "Organic Syntheses," Coll. Vol. I, p. 23, 1932, John Wiley & Sons, Inc., New York.

[20] Rupe and Bürgin, *Ber.*, **43**, 178 (1910). See also v. Braun, *ibid.*, **43**, 2842 (1910); and Grignard, Bellot and Courtot, *Ann. chim.*, [9] **12**, 366 (1920).

this olefin by alkaline potassium permanganate gave benzoic acid (m. p. 121–122°), thus showing the absence of any appreciable amount of a bicyclic compound.

Ozonolysis of the Olefin.—A solution of 4.8 g. of the olefin in 50 cc. of low-boiling petroleum ether was cooled to 0°, and ozone from a Berthelot ozonizer was bubbled through to saturation (thirty hours). The solvent was allowed to evaporate spontaneously at room temperature and the residual oily ozonide was refluxed with 50 cc. of water containing some zinc dust.

The aqueous solution was filtered, and from a portion of the filtrate a semicarbazone was obtained which was crystallized by dissolving in boiling alcohol and adding water to incipient turbidity. It formed small colorless plates of m. p. 126°. The m. p. of **hydrocinnamaldehyde semicarbazone** is given in the literature[21] as 125 or 127°. A sample we prepared ourselves from authentic hydrocinnamaldehyde melted at 125°. Mixed with the semicarbazone from the ozonolysis liquor, the m. p. was 124.5°.

Another portion of the aqueous filtrate was distilled and the first runnings were digested with benzaldehyde and alcoholic sodium hydroxide. Yellow crystals resulted of m. p. 110–111°. Mixed with an authentic sample of dibenzalacetone, the m. p. was 109–110°.

Still another portion of the aqueous filtrate was examined for the presence of formaldehyde by the resorcin-sulfuric acid test. The result was negative.

Attempts to prepare a pure dibromide from the olefin were unsatisfactory.

2-Methyl-5-phenylpentanol-3 (XV) was obtained by a Grignard synthesis from phenethyl bromide (111 g.) and isobutyraldehyde, as a colorless viscous liquid, of rose-type odor; b. p. 130.5–131.5° at 10 mm., 138–142° at 13 mm.; d_4^{25} 0.9563; n_D^{25} 1.50466; M_D obs. 55.22, calcd. 55.54; yield, 59.5% (57 g.).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.11; H, 10.32.

1,1-Dimethyltetralin (XI). (1) **From the tertiary alcohol (X).**—The cyclodehydration was effected as described for ionene, except that it was found more satisfactory to steam-distil the diluted hydrocarbon–acid mixture and recover the hydrocarbon from the distillate. The product was a colorless liquid whose odor resembled that of tetralin and of ionene; b. p. 98° at 10 mm., 220–222° at 761 mm.; d_4^{25} 0.9474; n_D^{25} 1.52736; M_D obs. 51.99, calcd. 51.82; yield, 82.5%, or 26.4 g. from 35.6 g. of the alcohol. Toward permanganate, or a carbon tetrachloride solution of bromine, the product behaved like a saturated compound. There was no evidence of any polymerization having occurred during the reaction.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.59; H, 9.96.

Dinitro Derivative.—Prepared in the same way as Bogert and Fourman[4] used for dinitroionene, the product formed colorless crystals, m. p. 64.5°; yield, 32%.

Anal. Calcd. for $C_{12}H_{14}O_4N_2$: N, 10.93. Found: 11.20.

Sulfonamide.—Using the method of Bogert and Fourman[4] for ionene sulfonamide, this lower homolog was crystallized by dissolving it in boiling acetone, adding water until the solution clouded and then cooling. It formed small colorless plates, m. p. 148–149°; yield, 33%.

Anal. Calcd. for $C_{12}H_{17}O_2NS$: N, 5.87; S, 13.39. Found: N, 6.05; S, 13.12.

A small amount of an isomeric sulfonamide was also isolated, m. p. 111°.

Anal. Calcd. for $C_{12}H_{17}O_2NS$: N, 5.87; S, 13.39. Found: N, 6.40; S, 13.12.

(2) **From the Olefin (XII).**—To 5 g. of the olefin, cooled in an ice-water bath, there was added gradually 10 cc. of 90% sulfuric acid, the more dilute acid being employed because no dehydration was involved in the reaction. The upper layer of the resultant mixture possessed a characteristic tetralin odor. It was separated, neutralized with a 10% sodium carbonate solution, washed and dried; yield, 4.5 g., or 90%.

Dinitro derivative, m. p. 64.5°: mixed with the dinitro derivative from (1) above, the m. p. was 64–64.5°.

(3) **From the Secondary Alcohol (XV).**—The cyclodehydration was carried out as in (1) above, and there resulted, from 26.7 g. of the alcohol, 17.9 g. (or 74.5%) of the dimethyltetralin, b. p. 98° at 10 mm.

Dinitro derivative, m. p. 64.5°: mixed with the dinitro derivative from (1), the m. p. was 64.5°.

Attempted Dehydrogenation of 1,1-Dimethyltetralin.—Attempts to dehydrogenate this hydrocarbon by heating with either sulfur or selenium were unsuccessful. It is possible that this may have been due to the relatively low b. p. (220–222°) of the compound, which prevented its remaining long in contact with the molten sulfur or selenium, except in the vapor phase. A higher temperature is probably necessary when, as in this case and with ionene, the reaction involves not only the elimination of hydrogen but of one of the *gem*-dimethyl groups as well. Should the experiments be repeated, they will be carried out under increased pressure and at higher temperature.

Oxidation of 1,1-Dimethyltetralin.—Oxidation of this hydrocarbon with alkaline permanganate gave a 22% yield of an acid which melted constantly at 117–118° when heated gradually, or at 123° when heated rapidly. Gabriel[22] reported the m. p. of α,α'-dimethylhomophthalic acid as 123° "bei schnellem Erwärmen." Distilled under reduced pressure, an anhydride passed over, m. p. 81°. Mixed with an authentic sample of α,α'-dimethylhomophthalic anhydride, the m. p. remained unchanged at 81°. Gabriel[23] has recorded the m. p. of α,α'-dimethylhomophthalic anhydride as 82.5–83°.

The results of this oxidation were the same in all cases, irrespective of whether the initial 1,1-dimethyltetralin was prepared by method (1), (2) or (3) above.

Summary

1. That ionene is 1,1,6-trimethyltetralin, as deduced by Bogert and Fourman, is now further proven by its synthesis from *m*-xylene.

2. A study of the synthesis of 1,1-dimethyl-

---

(21) (a) Michael and Garner, *Am. Chem. J.*, **35**, 266 (1906); (b) Bouveault, *Bull. soc. chim.*, [3] **31**, 1327 (1904).

(22) Gabriel, *Ber.*, **20**, 1200 (1887).

(23) Gabriel, *ibid.*, **19**, 2366 (1886).

tetralin makes it seem probable that the cyclodehydration of aralkanols to polynuclear hydrocarbons proceeds through intermediate formation of the aralkene with subsequent isomerization (cyclization) of the latter.

NEW YORK, N. Y. RECEIVED JANUARY 8, 1934

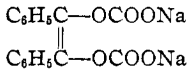
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Preparation and Reactions of Benzil-disodium

BY W. E. BACHMANN

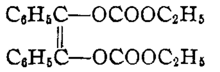
Beckmann and Paul[1] found that only one atom of sodium reacted with a molecule of benzil, $C_6H_5COCOC_6H_5$, and gave a violet colored solid; Nef[2] obtained the same product and considered that it was a molecular complex formed from a molecule each of benzil and benzil-disodium while Schlenk and Thal[3] believed it was a free radical. Staudinger and Binkert[4] were able to obtain benzil-dipotassium by heating a benzene solution of benzil with metallic potassium. We have now found a convenient method for preparing benzil-disodium, $C_6H_5C(ONa){=}(NaO)CC_6H_5$, which has not been obtained previously; the disodium compound is formed by interaction of benzil and 2% sodium amalgam at room temperature in a mixture of ether and benzene. During the reaction the violet colored complex is formed as an intermediate and then gives way to the orange colored crystals of the disodium derivative. In like manner anisil, 4,4′-diphenylbenzil and α-naphthil are converted to the disodium derivatives by the action of sodium amalgam; anisil gives a violet complex corresponding to addition of one atom of sodium and then a yellow disodium derivative; 4,4′-diphenylbenzil gives a blue intermediate and then a brown-red compound; the intermediate compound obtained from α-naphthil is red-brown while the disodium derivative is red.

Benzil-disodium reacts readily with a number of reagents. Like the benzil-dipotassium compound of Staudinger and Binkert and the iodomagnesium compound of Gomberg and Bachmann,[5] benzil-disodium gives benzoin when it is treated with water and in practically quantitative yield; anisoin, 4,4′-diphenylbenzoin and α-naphthoin are obtained by hydrolysis of the disodium derivatives of the corresponding benzils. Oxygen of the air oxidizes benzil-disodium at room temperature; hydrolysis of the product gives benzoic acid and some benzilic acid. Although Beckmann and Paul reported that the violet complex of benzil-disodium and benzil did not react with carbon dioxide, we have found that carbon dioxide is readily absorbed by benzil-disodium; in the reaction apparently the sodium salt of stilbenedicarbonic acid (I) is formed; when treated with water the salt is decomposed with loss of carbon dioxide and benzoin is formed. The stable diethyl ester (II) of this acid is obtained by interaction of benzil-disodium and chloroethylcarbonate. This ester is readily hydrolyzed to benzoin by dilute alkali.



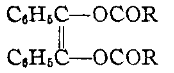
$$\begin{matrix} C_6H_5C\text{—}OCOONa \\ \| \\ C_6H_5C\text{—}OCOONa \end{matrix}$$

I



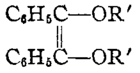
$$\begin{matrix} C_6H_5C\text{—}OCOOC_2H_5 \\ \| \\ C_6H_5C\text{—}OCOOC_2H_5 \end{matrix}$$

II



$$\begin{matrix} C_6H_5C\text{—}OCOR \\ \| \\ C_6H_5C\text{—}OCOR \end{matrix}$$

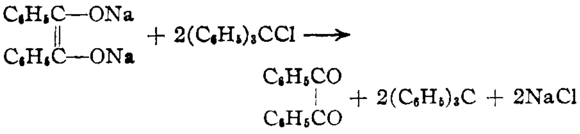
III



$$\begin{matrix} C_6H_5C\text{—}OR' \\ \| \\ C_6H_5C\text{—}OR' \end{matrix}$$

IV

Esters of dihydroxystilbene are formed by treatment of the benzil-disodium with acid chlorides or anhydrides; with acetic anhydride stilbenediacetate (III, $R = CH_3$) is formed; benzoyl chloride gives stilbenedibenzoate (III, $R = C_6H_5$) and *p*-toluyl chloride yields stilbene-di-*p*-toluate (III, $R = C_6H_4CH_3$-*p*). Ethers are obtained by interaction of the disodium compound with alkyl halides; in this respect the disodium compound is more reactive than the iodomagnesium derivative. Methyl iodide gives stilbenedimethyl ether (IV, $R' = CH_3$), while allyl bromide yields stilbenediallyl ether (IV, $R' = CH_2CH{=}CH_2$). Triphenylchloromethane reacts rapidly with benzil-disodium but does not give an ether; instead benzil and triphenylmethyl are formed. In a



$$\begin{matrix} C_6H_5C\text{—}ONa \\ \| \\ C_6H_5C\text{—}ONa \end{matrix} + 2(C_6H_5)_3CCl \longrightarrow \begin{matrix} C_6H_5CO \\ | \\ C_6H_5CO \end{matrix} + 2(C_6H_5)_3C + 2NaCl$$

---

[1] Beckmann and Paul, *Ann.*, **266**, 1 (1891).

[2] Nef, *ibid.*, **308**, 287 (1899).

[3] Schlenk and Thal, *Ber.*, **46**, 2850 (1913).

[4] Staudinger and Binkert, *Helv. Chim. Acta*, **5**, 703 (1922).

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