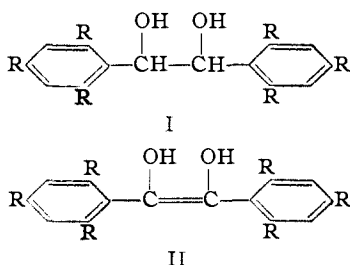


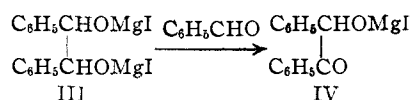
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Bimolecular Reduction of Hindered AldehydesBY REYNOLD C. FUSON, E. C. HORNING,¹ M. L. WARD, S. P. ROWLAND AND J. L. MARSH

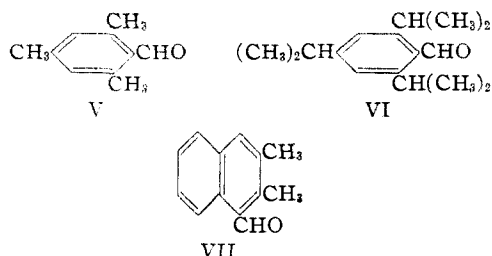
Hydrobenzoins of type I have taken on added significance because of their close structural relationship with the corresponding stilbenediols (II).² A number of such hydrobenzoins have now



been synthesized and studied. The best method of preparation is the bimolecular reduction of the corresponding aldehydes, and the most effective reagent for this purpose appears to be the binary mixture of Gomberg and Bachmann.³ When this reagent was used with benzaldehyde,⁴ the primary product was the hydrobenzoinate (III), but the benzaldehyde present oxidized it rapidly to the benzoinate (IV).

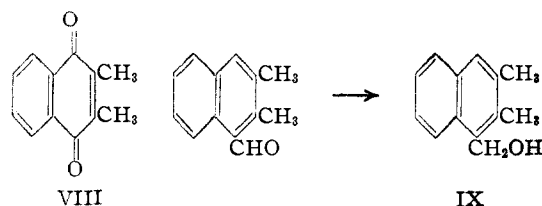


Highly hindered benzaldehydes do not oxidize the hydrobenzoinate. Hindrance in the hydrobenzoinate molecule has the same effect, for the iodomagnesium isohydromesitoinate is unaffected by benzaldehyde. Hence, in the reduction of highly hindered benzaldehydes, the process is interrupted at the hydrobenzoin stage. In the present work a study has been made of the bimolecular reduction of mesitaldehyde (V), 2,4,6-triisopropylbenzaldehyde (VI) and guaialdehyde (VII).



Several methods were employed in the synthesis of mesitaldehyde. The most satisfactory of these is that of Gattermann⁵ as modified by Adams and Montgomery⁶ for phenol and phenol ethers. By raising the reaction temperature to 70° and using tetrachloroethane as solvent, the yield of aldehyde was increased from 35–40% to 82.5%. When applied to 1,3,5-triethylbenzene, 1,3,5-triisopropylbenzene and guaiene, this procedure gave yields of 70, 65 and 38%, respectively, of the corresponding aldehydes. 2,4,6-Triethylbenzaldehyde, 2,4,6-triisopropylbenzaldehyde and guaialdehyde were new compounds. 2,4,6-Triethylbenzaldehyde was converted by air oxidation to the known 2,4,6-triethylbenzoic acid.⁷ The semicarbazone and 2,4-dinitrophenylhydrazones were formed. The physical constants and analytical data for these and other new compounds reported in this paper are to be found in the table. 2,4,6-Triisopropylbenzaldehyde was converted by oxidation into the known 2,4,6-triisopropylbenzoic acid.⁸ Hydrogenation of the aldehyde yielded the corresponding benzyl alcohol. The semicarbazone of the aldehyde was also prepared.

Guaialdehyde was characterized by conversion to the known⁹ 1,2,3-trimethylnaphthalene. Oxidation with perhydrol in glacial acetic acid¹⁰ converted guaialdehyde into guaioquinone (VIII).¹¹ Aluminum isopropoxide reduced the aldehyde to guaiylcarbinol (IX).



In each instance reduction with the binary mixture transformed the aldehyde into a mixture of the two theoretically possible diastereoisomeric glycols. The glycols from mesitaldehyde and

(5) Gattermann, *Ann.*, **357**, 313 (1907); Hinkel, Ayling and Beynon, *J. Chem. Soc.*, 339 (1936).

(6) Adams and Montgomery, *THIS JOURNAL*, **46**, 1518 (1924).

(7) Fuson and Corse, *ibid.*, **60**, 2063 (1938).

(8) Fuson and Horning, *ibid.*, **62**, 2962 (1940).

(9) Ruzicka, Keller and Stütze, *Helv. Chim. Acta*, **15**, 143 (1932).

(10) Arnold, *J. Org. Chem.*, **5**, 250 (1940).

(11) Wieser, *Monatsh.*, **1**, 604 (1880).

(1) Du Pont Fellow in Chemistry, 1939–1940.

(2) Fuson, McKeever and Corse, *THIS JOURNAL*, **62**, 600 (1940).

(3) Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

(4) Gomberg and Bachmann, *ibid.*, **52**, 4967 (1930).

2,4,6-triisopropylbenzaldehyde were accompanied by smaller amounts of unsaturated compounds, which proved to be the corresponding hexaalkylstilbenes. This appears to be the first example of the production of an unsaturated compound by the use of the magnesium-magnesium iodide reagent.

The structure of the glycols follows from their reactions. They gave diacetates when treated with acetic anhydride and in two cases were reduced to the corresponding ethanes. Further, the high-melting glycol from mesitaldehyde was made by an entirely different method—high pressure hydrogenation of mesitoin.

Experimental

Synthesis of the Aldehydes.—The modified Gattermann synthesis that was developed for the aldehydes may be illustrated by that used in making 2,4,6-triisopropylbenzaldehyde.

A rapid stream of dry hydrogen chloride was passed into a mixture of 100 g. of 1,3,5-triisopropylbenzene,¹² 102 g. of zinc cyanide and 400 cc. of tetrachloroethane until the cyanide was decomposed. The mixture was cooled to 0° and to it was added 134 g. of aluminum chloride with vigorous stirring. Introduction of hydrogen chloride was resumed and continued for eight hours at 70°. The mixture was poured into an ice and hydrochloric acid mixture and allowed to stand overnight. It was then heated under reflux for three hours. The aldehyde was isolated by distillation. The yield was 75 g.

Mesitaldehyde, 2,4,6-triethylbenzaldehyde and guaialdehyde were prepared in a similar manner. Mesitaldehyde was found to melt at 10.5°; b. p. 124–128° (15 mm.); d_{20}^{20} 1.0987; n_D^{20} 1.5524.

2,4,6-Triisopropylbenzyl Alcohol.¹³—Twenty-three grams of 2,4,6-triisopropylbenzaldehyde was treated with hydrogen for ten hours over copper chromite at a pressure of 2600 lb. and a temperature of 200°. No solvent was used. The carbinol was purified by recrystallization.

1,2,3-Trimethylnaphthalene.—Guaialdehyde (9.2 g.) was hydrogenated over Raney nickel (2 g.). Its ethanol solution reacted rapidly at 150° under 1400 lb. hydrogen pressure. After removal of catalyst and solvent, the product distilled at 255–265° under atmospheric pressure. The refractive index of the distillate (n_D^{21} 1.543) showed that a dihydrotrimethylnaphthalene had been produced.

One-tenth gram of palladium-on-norite catalyst was added to 1.0 cc. of this distillate. At 250° the evolution of hydrogen was complete in one-half hour.

The dehydrogenation product was identified as 1,2,3-trimethylnaphthalene by preparation of the known picrate and styphnate⁹ (melting points 142.5–145° and 145–146°, respectively). Absolute ethanol was used as solvent for the preparation and crystallization of these derivatives.

Guaioquinone.—One gram of guaialdehyde was treated with perhydrol under the conditions used by Arnold.¹⁰

There resulted 0.49 g. of guaioquinone, melting in the range 123–126°.

Similar treatment of the lower-melting hydroguaioin also produced the quinone. The impurities in this product were not easily removed by crystallization. Zinc dust and acetic anhydride transformed the quinone to hydroguaioquinone diacetate which was easily purified; m. p. 192–194°.¹⁴

Bimolecular Reduction of the Aldehydes.—The procedure may be illustrated by that employed in the reduction of mesitaldehyde. The binary mixture was prepared in the usual manner from 15 g. of magnesium turnings, 100 cc. of dry ether, 150 cc. of dry benzene and 60 g. of iodine. A solution of 67 g. of mesitaldehyde in 75 cc. of dry benzene was run from the separatory funnel into the reaction flask over a period of one and a half hours. The mixture was stirred vigorously and refluxed for twelve hours. The product was isolated in the usual manner. The solid was warmed with high-boiling petroleum ether and the undissolved material was separated and recrystallized from methanol. This yielded the glycol melting at 214–215°.

The solvent was removed from the petroleum ether solution and the residue recrystallized from methanol. In this way it was possible to obtain a solid, melting at 132–133°, which proved to be the stilbene, 1,2-dimesitylethylene. The filtrate was evaporated to dryness and the residue crystallized from high-boiling petroleum ether. This solid melted at 160–161° and was identified as the low-melting glycol, isohydromesitoin. The high- and low-melting glycols were obtained in yields of 13 g. and 36 g., respectively. The yield of the stilbene was 1.2 g.

The two glycols were treated with methylmagnesium iodide in the Grignard machine and each gave two moles of gas.

The high-melting glycol was also made by hydrogenation of mesitoin at 125° and 2300 lb. pressure of hydrogen. A mixture of 1 g. of mesitoin, 19 cc. of alcohol and 2 g. of copper chromite catalyst was treated with hydrogen under these conditions for fifty minutes. The glycol crystallized from aqueous acetone in long needles melting at 214–215°, which were shown to be identical with those prepared by bimolecular reduction of mesitaldehyde.¹⁵

Acetylation of the Glycols.—Treatment of hydromesitoin with acetic anhydride and pyridine converted it into the corresponding acetate, melting at 181–182°. When hydrolyzed with aqueous sodium hydroxide, the acetate was reconverted to hydromesitoin. The low-melting glycol, isohydromesitoin, when acetylated, yielded an acetate melting at 124–125° from which it could be regained by hydrolysis.

1,2-Dimesitylethane.—A mixture of 1.5 g. of the low-melting glycol from mesitaldehyde, 2 g. of copper chromite catalyst and 19 cc. of absolute alcohol was subjected for two hours to a temperature of 250° at a pressure of 2000 lb. of hydrogen. The product melted at 117–117.5° and was shown by the mixed melting point method to be 1,2-dimesitylethane.¹⁶

1,2-Di-(2,4,6-triisopropylphenyl)-ethane.—A mixture of 0.5 g. of the high-melting glycol from 2,4,6-triisopropyl-

(12) Alkazene-13 from the Dow Chemical Company was used.

(13) The high-pressure hydrogenations reported in this article were carried out by Dr. J. F. Kaplan and Mr. J. C. Robinson, Jr.

(14) Crawford, *THIS JOURNAL*, **57**, 2002 (1935).

(15) This experiment was carried out by Dr. J. W. Corse.

(16) Wenzel, *Monatsh.*, **35**, 954 (1914).

TABLE I

Compound	Melting point, °C.	Solvent	Analyses, %			
			C	Calcd.	H	Found
$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{MesCH}-\text{CHMes}^a \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	214-215	Methanol	80.48	8.78	80.62	8.79
$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{MesCH}-\text{CHMes} \\ \quad \\ \text{CH}_3\text{COO} \quad \text{OCOCH}_3 \end{array}$	160-161	High-boiling pet. ether	80.48	8.78	80.58	8.78
$\begin{array}{c} \text{MesCH}-\text{CHMes} \\ \quad \\ \text{CH}_3\text{COO} \quad \text{OCOCH}_3 \end{array}$	181-182	Methanol	75.35	7.91	75.56	7.83
$\begin{array}{c} \text{MesCH}-\text{CHMes} \\ \quad \\ \text{MesCH}=\text{CHMes} \end{array}$	124-125	Methanol	75.35	7.91	75.42	8.04
$\begin{array}{c} \text{MesCH}=\text{CHMes} \\ \text{TepCHO}^b \end{array}$	132-133	Methanol	90.84	9.16	90.74	9.21
$\begin{array}{c} \text{TepCH}=\text{NNHC}_6\text{H}_5(\text{NO}_2)_2 \\ \text{TepCH}=\text{NNHCONH}_2 \end{array}$	180-181 155-156	Ethyl acetate-ethanol Ethanol-water	82.05 62.11 67.98	9.53 6.03 8.56	81.87 61.77 67.93	9.59 6.02 8.41
$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{TipCH}-\text{CHTip} \\ \quad \\ \text{TipCHO}^c \end{array}$	285-286	High-boiling pet. ether	82.40 82.69	10.73 10.42	82.42 82.40	10.57 10.40
$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{TipCH}-\text{CHTip} \\ \quad \\ \text{CH}_3\text{COO} \quad \text{OCOCH}_3 \end{array}$	186-187	Low-boiling pet. ether	82.40	10.73	82.16	10.82
$\begin{array}{c} \text{TipCH}-\text{CHTip} \\ \quad \\ \text{CH}_3\text{COO} \quad \text{OCOCH}_3 \end{array}$	201-202	Methanol	78.48	9.88	78.61	9.88
$\begin{array}{c} \text{TipCH}-\text{CHTip} \\ \quad \\ \text{TipCH}=\text{NNHCONH}_2 \end{array}$	160-161 150-151	Methanol Ethanol (20%)	78.48 70.55	9.88 9.42	78.29 70.40	9.76 9.28
$\begin{array}{c} \text{TipCH}_2\text{OH} \\ \text{TipCH}=\text{CHTip} \end{array}$	83-84 147-148	Ethanol Methanol	82.05 88.88	11.11 11.11	81.97 89.14	11.23 10.99
$\begin{array}{c} \text{TipCH}_2\text{Cl}^d \\ \text{TipCH}_2\text{CH}_2\text{Tip} \end{array}$ 160-161 Benzene-ethanol	76.05 88.39	9.90 11.60	76.07 88.50	10.07 11.68
$\begin{array}{c} \text{Dibromide} \\ \text{GuaiCHO}^e \\ \text{GuaiCH}=\text{NNHCONH}_2 \end{array}$	199-200 77.5-78.5 265 d.	Benzene-ethanol Ethanol-water Ethanol-water	64.84 84.75 69.78	8.16 6.56 6.27	64.98 85.04 69.78	8.21 6.87 6.23
$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{GuaiCH}-\text{CHGuai} \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	162-163.5	Methanol-water ^f	84.28	7.06	84.53	7.31
$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{GuaiCH}-\text{CHGuai} \\ \quad \\ \text{CH}_3\text{COO} \quad \text{OCOCH}_3 \end{array}$	274-275.5 (uncor.)	Toluene	84.28	7.06	84.64	7.08
$\begin{array}{c} \text{GuaiCH}-\text{CHGuai} \\ \quad \\ \text{CH}_3\text{COO} \quad \text{OCOCH}_3 \end{array}$	198-199	Ethanol-water	79.26	6.66	78.94	6.73
$\begin{array}{c} \text{GuaiCH}-\text{CHGuai} \\ \quad \\ \text{GuaiCH}_2\text{OH}^g \end{array}$	290-293 (uncor.) 114-115	Acetic acid Ethanol-water	79.26 83.83	6.66 7.58	78.88 83.55	6.73 7.92

^a Mesityl, 2,4,6-triethylphenyl, 2,4,6-triisopropylphenyl and guaiyl are represented, respectively, by Mes, Tep, Tip and Guai. ^b Boiling point 146-149° (21 mm.). ^c Boiling point 123-125° (4 mm.); n_D^{20} 1.5132; d_4^{20} 0.9345. ^d Boiling point 129-130° (4 mm.); n_D^{20} 1.5151. ^e The aldehyde mixture produced from guaiene was 80% of the calcd.; b. p. 165-168° (4 mm.); m. p. 62-66°. Crystallization from high-boiling petr. ether or from ethanol-water mixture produced pure guai aldehyde in 38% yield. ^f The separation of hydroguaioin from isohydroguaioin was based on the great difference in their solubility in methanol. The latter was 300 times as soluble as the former in this solvent. ^g The interaction of guai aldehyde and aluminum isopropoxide was brought about in refluxing benzene solution

benzaldehyde, 20 cc. of alcohol and 1.0 g. of copper chromite catalyst was heated for twelve hours at 250° and 6000 lb. pressure of hydrogen. The hydrocarbon was purified by recrystallization. The same compound was obtained by a similar treatment of the low-melting glycol.

The ethane was also made by coupling 2,4,6-triisopropyl-

benzyl chloride by the action of methylmagnesium iodide. A solution of methylmagnesium iodide was made from 7 g. of magnesium and 40 g. of methyl iodide. To it was added gradually 25 g. of 2,4,6-triisopropylbenzyl chloride (see below) in 30 cc. of absolute ether. The ethane was isolated in the usual way.

Bromination in chloroform converted the ethane to a dibromide—presumably 1,2-di-(2,4,6-triisopropyl-3-bromophenyl)-ethane. It was purified by recrystallization.

2,4,6-Triisopropylbenzyl Chloride.¹⁷—This compound was prepared in 85% yields by the general method of Sommelet.¹⁸ A mixture of 300 g. of triisopropylbenzene, 200 g. of chloromethyl ether and 600 cc. of carbon disulfide was cooled to 0°, and 120 g. of stannic chloride was added gradually, with stirring, over a period of one hour. The mixture was stirred for an additional hour and poured on ice. The chloromethyl compound was purified by distillation.

(17) This compound was prepared by Mr. Norman Rabjohn.

(18) Sommelet, *Compt. rend.*, **157**, 1443 (1913).

Summary

An improved method has been developed for the synthesis of mesitaldehyde. The procedure has been used successfully to prepare 1,3,5-triethylbenzaldehyde, 1,3,5-triisopropylbenzaldehyde and guaialdehyde.

Mesitaldehyde, 2,4,6-triisopropylbenzaldehyde and guaialdehyde have been reduced bimolecularly to yield the corresponding hydrobenzoins.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Alkylation of Paraffins at Low Temperatures in the Presence of Aluminum Chloride

BY HERMAN PINES, ARISTID V. GROSSE AND V. N. IPATIEFF

The alkylation^{1,2,3} of isobutane with propene and butene in the presence of aluminum chloride was studied at temperatures ranging from -40° to +150°. At the lower temperatures it was possible to carry out this reaction at atmospheric pressure, while at 0° or higher the experiments were made under increased pressure. This paper will deal only with the low temperature alkylation.

For the low temperature alkylation, a continuous-operation glass apparatus was designed with which it was possible to regulate the temperature, contact time or feed rate.

Discussion of Results

The properties of the products obtained from the reaction of olefins with paraffins in the presence of aluminum chloride-hydrogen chloride depend on several factors: concentration of olefins, temperature, time of contact, and quantities of hydrogen chloride used. When the charging stock contains a large proportion of olefins, the resulting product is of a high molecular weight; it was found that when a ratio of 4 parts of paraffins to 1 part of olefins is used, the resultant product is of the desired properties. The temperature and experimental conditions depend upon the pair of hydrocarbons used. Ethene reacts with paraf-

fins at 0° or higher and, therefore, the experiments are preferably made under super-atmospheric pressure. For other olefins, temperatures ranging from -45° to room temperature produce satisfactory results. Very low temperatures (-100°) are not desired, since at these temperatures the paraffinic hydrocarbons are not very reactive, and the resulting product consists of high-boiling hydrocarbons due to the polymerization of olefins.

The aluminum chloride was always observed to undergo a series of changes. The fine suspended aluminum chloride first formed flocculent curds that later formed hard pieces; after a period of time these pieces softened into a heavy sticky gum which slowly became a yellow-brown viscous liquid. When the catalyst reached this stage, great difficulty was encountered in keeping the discharge tube open. In some cases plugging of the discharge tube occurred, and the experiment had to be discontinued, although the aluminum chloride showed no diminution in activity.

Isobutane-*n*-Butenes.—As an example of a continuous alkylation of isobutane with *n*-butene, a typical experiment is described in detail in Table I in the experimental part. This reaction was made at -35° in an atmospheric-pressure, continuous-alkylation apparatus (Figs. 1 and 2). The liquid product resulting from this reaction contained over 60% of octanes and 12% dodecanes. About 90% of the total product distilled below 225° and consisted of paraffinic hydrocarbons only. The exit gases did not contain any olefinic hydrocarbons; they consisted only of un-

(1) V. N. Ipatieff and H. Pines, U. S. Patents 2,112,846 and 2,112,847, April 5, 1938.

(2) (a) V. N. Ipatieff "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Company, New York, N. Y., 1937, p. 673; (b) V. N. Ipatieff, A. V. Grosse, H. Pines and V. I. Komarewsky, *ibid.*, **58**, 913 (1936); (c) H. Pines, paper presented before the Division of Organic Chemistry at the American Chemical Society Meeting, Dallas, Texas, April, 1938.

(3) V. N. Ipatieff and A. V. Grosse, *Ind. Eng. Chem.*, **28**, 461 (1936).