V. Hobbs and J. Sorensen who carried out the microanalyses for carbon, hydrogen and nitrogen

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The Arylmethylation of Benzene Derivatives

BY CLARK M. WELCH AND HILTON A. SMITH

The acid-catalyzed condensation of paraformaldehyde with a number of substituted benzenes to produce substituted diphenylmethanes has been studied. Conditions have been found under which good yields (up to 86%) of the diphenylmethanes are obtained. It has also been shown that further condensation to form substituted dihydroanthracenes is possible.

The acid-catalyzed condensation of a number of aromatic compounds with formaldehyde or formaldehyde derivatives is known to yield diarylmethanes under the proper conditions. This reaction is similar to the process of chloromethylation studied in a previous publication,¹ the benzyl type of carbonium ion being a possible intermediate in both processes. The similarity of the two reactions is borne out by the frequent appearance of diarylmethanes as by-products in chloromethylations.

The arylmethylation reaction is known chiefly for such reactive benzene derivatives as the phenols and arylamines. A smaller number of the less reactive compounds have been studied, examples being benzene,² toluene,³ benzyl chloride,⁸ diphenyl,³ iodobenzene,⁴ naphthalene⁵ and mesitylene.⁶ In most of this early work the yields were not reported. The preparative value of the reaction appeared in later studies on the reaction of benzene with formalin to give 70–76% yields of diphenylmethane.⁷

In these examples the formaldehyde was used in a variety of forms such as formalin, paraformaldehyde, methylal, trioxymethylene and methylene diacetate. Sulfuric acid, often with a diluent, was used as the catalyst.

The present studies were made to determine further applications and limitations of the reaction when used with non-phenolic and non-aminated derivatives of benzene. A variety of polyalkylbenzenes, a polyhalobenzene, and a polyalkyldiphenylmethane were condensed with paraformaldehyde in the presence of sulfuric acid. The aromatic compounds were chosen having such a configuration as would permit the formation of only a single isomer in the product. A diluent for the acid was found to be necessary in order to prevent excessive sulfonation of the compounds. For this purpose 95% ethanol was usually employed since previous work^{7a,3} indicates the presence of alcohols to be advantageous. The results appear in Table I.

C. D. Shacklett and H. A. Smith, THIS JOURNAL, 73, 766 (1951).
A. Baeyer, Ber., 6, 221 (1873).

(3) J. Weiler, *ibid.*, 7, 1181 (1874); T. Reichstein and K. Oppenauer, *Helv. Chim. Acta*, 16, 1373 (1933).

(4) A. M. Nastukov and V. V. Shelyagin, J. prakt. Chem., 119, 303 (1928).

(5) J. Grabowski, Ber., 7, 1605 (1874).

(6) A. Baeyer, *ibid.*, 5, 1098 (1872).

(7) (a) N. K. Moshchinskaya and R. L. Globus, J. Applied Chem. (U. S. S. R.), 17, 76 (1944); (b) ibid., 17, 137 (1944).

 $(8)\,$ W. H. Bentley and B. Catlow, British Patent 446,450 (April 30, 1936).

In addition to the above syntheses, unsuccessful attempts were made to condense p-toluic acid with paraformaldehyde. Reaction other than esterification occurred only at high concentrations of sulfuric acid and resulted chiefly in sulfonation.

These results show that many benzene derivatives whose substituents are o- and p- directing (even though they may be deactivating) can be converted to the diarylmethanes in good yield. The reaction is free from rearrangements and extensive tar formation, and the products are readily purified. Except for bis-(2,4,6-trimethylphenyl)-methane, none of these diarylmethanes had been previously prepared in yields exceeding 15% of theory based on the benzene derivative. Bis-(2,4,6-trimethylphenyl)-methane had been prepared in 50% over-all yield from bromomesitylene by means of a four-step synthesis, involving the preparation of dimesityl ketone.⁹ Bis-(2,4,6-triisopropylphenyl) - methane and bis - (2,4 - dichlorophenyl)-methane are new compounds.

An interesting extension of the method is seen in the further condensation of bis-(1,2,3,4-tetramethylphenyl)-methane with paraformaldehyde to give 1,2,3,4,5,6,7,8-octamethyl-9,10-dihydroanthracene. The over-all yield based on 1,2,3,4-tetramethylbenzene was 52%. The compound had been previously prepared in three steps from 2,3dimethylhexadiene-2,4 by means of a Diels-Alder condensation, resulting in an over-all yield of 25%.¹⁰ Selenium dehydrogenation of the product gave 1,2,3,4,5,6,7,8-octamethylanthracene as described by these workers. The formation of anthracenes as by-products in condensations using formaldehyde has also been noted.¹¹

The slow reaction and low yield obtained in preparing bis-(triisopropylphenyl)-methane is indicative of the great steric hindrance present in 1,3,5-triisopropylbenzene. The latter is electronically analogous to 1,3,5-trimethylbenzene, a compound which gave good yields. The inertness of p-toluic acid shows that meta-directing groups have a strong suppressive action with respect to arylmethylation.

The side reactions observed in these preparations were sulfonation and polymer formation. Both reactions were minimized by the use whenever possible of low acid concentration, low reaction

(9) E. P. Kohler and R. Baltzly, THIS JOURNAL, 54, 4015 (1932).

(10) H. J. Bacher, J. Strating and L. H. H. Huisman, *Rec. trav. chim.*, 58, 761 (1939).
(11) Son for example, J. Thirle and H. Bethern, *Phys. Rev.* 77, 1467.

(11) See, for example, J. Thiele and H. Balborn, Ber., 37, 1467 (1904).

DIA	RYLMETHAN	NES AND	DERIVATIVES	5		
Aryl group	Acid concn. ^a	Reac- tion temp., °C.	B.p. (21 mm.), °C. cor.	M.p., °C. cor.	Previous m.p., °C.	Yield, i %
2,5-Dimethylphenyl-	1:2	95	185 - 187	60.9 - 62.1	$60.0-60.5^{d}$	56
2,4,6-Trimethylphenyl-	$1\!:\!2.5$	80	212 - 213	134.4 - 135.4	135°	67
2,3,5,6-Tetramethylphenyl-	1:2.5	95	238 - 241	155.7 - 156.7	157.5 - 158.0'	59
2,3,4,5-Tetramethylphenyl-	1:2.5	95	244 - 247	149.6 - 150.3	146-1479	85^{k}
Pentamethylphenyl-	1:2.5	75		220.6 - 221.2	$217 - 218^{f}$	86
2,4,6-Triisopropylphenyl-	1:1.33	95		69.4–70.0, 87.0–87.6		11^i
2,5-Dichlorophenyl-	8:1 ^b Anthrac	95 ene deri	221–225 vatives	83.7-84.7		6 0
1,2,3,4,5,6,7,8-Octamethyl-9,10-dihydro- ^c 1,2,3,4,5,6,7,8-Octamethyl-	1:2	80		284.5–285.5 297.8–298.6	283–284 ^h 299–300 ^h	61 ^k

TABLE I DIARVLMETHANES AND DERIVATIVES

^a The ratio of 96% sulfuric acid to 95% ethanol by volume. ^b The ratio of 96% sulfuric acid to water by volume. ^c Prepared from bis-(2,3,4,5-tetramethylphenyl)-methane and paraformaldehyde. ^d R. C. Huston and D. T. Ewing, THIS JOUR-NAL, **37**, 2397 (1915). ^e E. P. Kohler and R. Baltzly, *ibid.*, **54**, 4015 (1932). ^f I. I. Lapkin, J. Gen. Chem. (U. S. S. R.), **16**, 729 (1946). ^e C. L. Hewett and R. H. Martin, J. Chem. Soc., 1396 (1940). ^h H. J. Bacher, J. Strating and L. H. H. Huisman, *Rec. trav. chim.*, **58**, 761 (1939). ⁱ Based on paraformaldehyde. The excess benzene derivative was always recovered unchanged. Usually 3-10% of the product was material recovered from mother liquors and repurified. It melted 0.2-1.0° lower than the tabulated values. ^j Reaction was only 50% complete. ^k Based on benzene derivative.

temperature, and a short reaction time. The use of an excess of the benzene derivative also reduced the amount of polymer formation. Attempts to use p-toluenesulfonic acid as the catalyst were unsuccessful.

Experimental

Materials.—Eastman Kodak Company reagent grade paraformaldehyde, p-toluic acid, p-xylene and p-toluenesulfonic acid were used without further purification. Eastman reagent grade mesitylene and p-dichlorobenzene were redistilled prior to being used. The 1,3,5-triisopropylbenzene was obtained by twice redistilling in a 4-ft. Vigreux column a sample of "Alkazene 13" kindly furnished by the Dow Chemical Company. The main fraction distilled at 234.8-235.4° at 737 mm.

The durene, prehnitene and pentamethylbenzene were kindly furnished by Dr. C. D. Shacklett. They were prepared as previously described.¹

Analytical Methods.—The molecular weight determinations made on the products were carried out by the cryoscopic method using benzene as a solvent, or by the ebullioscopic method using a Menzies-Wright apparatus. Duplicate runs checked within 5% of each other, and were averaged to give the recorded values.

General Procedure for Polyalkyldiphenylmethanes.—In a 500-ml. 3-necked flask fitted with a reflux condenser, mechanical stirrer, and thermometer, and surrounded by a waterbath heated to the desired reaction temperature (Table I) were placed 0.67 mole of the polyalkylbenzene (1.0 mole for p-xylene and durene) and 0.17 mole of paraformaldehyde. In a separate beaker was placed 170 ml. of 95% ethanol. To this was cautiously added the proper amount of 96% sulfuric acid (Table I) by pouring the latter down the side of the beaker. The alcoholic solution was stirred, cooled to 5° below the desired reaction temperature, and then poured into the mixture of organic reagents in the flask. The heterogeneous mixture was stirred vigorously at the proper temperature for one hour.

The reaction mixture was then poured into 250 ml. of water. Then 250-300 ml. of benzene was added (ether was used for di-p-xylylmethane to facilitate recovery of excess xylene). The mixture was shaken, and the benzene layer was separated. The benzene extract was fractionated by distillation using a 10-inch Vigreux column. The benzene was distilled first, then the excess starting material (usually under reduced pressure), and finally the product at the temperature and pressure given in Table I. In the case of bis-(2,3,5,6-tetramethylphenyl)-methane and bis-(2,4,6-triiso-propylphenyl)-methane, distillation of the product fraction was carried out as detailed below.

The product was recrystallized as described below, other variations in the preparation being given also.

Bis-(2,5-dimethylphenyl)-methane was dissolved in hot 95% ethanol, treated with charcoal (Norite A), filtered while hot, concentrated, and the product recrystallized; mol. wt. obsd. 227, calcd. 224.

Bis-(2,4,6-trimethylphenyl)-methane was dissolved in hot benzene, treated with charcoal, filtered while hot, and to the filtrate was added two volumes of methanol to effect recrystallization; mol. wt. obsd. 259, calcd. 252.

Bis-(2,3,4,5-tetramethylphenyl)-methane was recrystallized from benzene-methanol in the same way. The identity of this compound was established by its conversion into two known derivatives (Table I), its melting point also checking that observed by previous workers.

Bis-(2,3,5,6-tetramethylphenyl)-methane was distilled twice from a Claisen flask having a take-off arm 12 mm. in inner diameter and sealed to the receiver. This arrangement prevented clogging of the take-off, which could be heated with a flame when necessary. The product was then recrystallized from benzene-methanol in the same way as dimesitylmethane; mol. wt. obsd. 275, calcd. 280.

Bis-(pentamethylphenyl)-methane was prepared using the following quantities of reagents: 1.00 g. (0.0067 mole) of hydrocarbon, 0.30 g. (0.01 mole) of paraformaldehyde, 8 ml. of 96% sulfuric acid, and 20 ml. of 95% ethanol. The reaction time was 30 minutes.

The reaction mixture was poured into 100 ml. of water and then filtered. The solid was dissolved in benzene, and recrystallized by adding methanol. After two such recrystallizations the product was recrystallized from dioxane; mol. wt. obsd. 310, calcd. 308.

Bis-(2,4,6-triisopropylphenyl)-methane was distilled in a Claisen flask until the head temperature reached 250° at 24 mm. The viscous liquid distillate was stirred with 5 ml. of ethanol until crystallization occurred. It was recrystallized four times. In some runs a low melting form (plates) was obtained, while in other runs a high melting form (aggregates of needles) resulted (Table I). A mixed melting point gave only the high value. The low melting form was converted to the stable high melting form by seeding its saturated ethanolic solution with the latter. Thus the compound has two crystalline modifications.

Anal.¹² Calcd. for $C_{31}H_{48}$: C, 88.50; H, 11.50. Found: C, 88.52; H, 11.41.

Bis-(2,5-dichlorophenyl)-methane was prepared using a reaction time of 3 hr. A 15-ml. quantity of water was used in place of the ethanol in the general procedure given above. The distilled product was recrystallized by seeding the warm ethanolic solution. If too high a crystallization temperature was used, the product came out as an oil which solidified on being cooled.

(12) Galbraith Microanalytical Laboratories, Box 32, Knoxville, Tennessee

Anal.¹² Calcd. for $C_{18}H_8Cl_4$: C, 51.01; H, 2.64. Found: C, 50.94; H, 2.58.

1,2,3,4,5,6,7,8-Octamethyl-9,10-dihydroanthracene.—In a 200-ml. flask set up as described in the general procedure were placed 14.0 g. (0.05 mole) of bis-(2,3,4,5-tetramethylphenyl)-methane, 4.5 g. (0.15 mole) of paraformaldehyde, and 20 ml. of carbon tetrachloride. A solution of 40 ml of 96% sulfuric acid in 80 ml. of 95% ethanol was added at 75° to this mixture, which was then stirred vigorously at 80° for 3 hr. The upper layer was then decanted, and the carbon tetrachloride slurry was filtered. The solid was stirred with methanol and again filtered. After two more washings with methanol, the solid was dissolved in 400 ml. of hot xylene and 2 g. of charcoal (Norite A) was added. The mixture was filtered while hot, the filtrate was concentrated to 200 ml., and slowly cooled to effect crystallization. The compound was converted to 1,2,3,4,5,6,7,8-octamethylanthracene by selenium dehydrogenation as previously described.¹⁰ The removal of selenium from the product was facilitated by repeated treatment of the hot chlorobenzene solution with charcoal. An attempt was made to prepare 1,2,3,4,5,6,7,8-octamethyl-9,10-dihydroanthracene directly from 1,2,3,4-tetramethylbenzene without isolating the intermediate diarylmethane. The product obtained in this way melted at $263-274^\circ$. It contained a large amount of impurities which were difficult to remove by recrystallization.

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Allylic Chlorides. XIV. The Preparation and Properties of *cis*- and *trans*-1,2,3-Trichloro-2-butene¹

By Lewis F. Hatch and John J. D'Amico

The following five new compounds have been synthesized and characterized: cis-1,2,3-trichloro-2-butene, trans-1,2,3-trichloro-2-butene, cis-2,3-dichloro-2-buten-1-ol, trans-2,3-dichloro-2-buten-1-ol and 2,3,3-trichloro-1-butene. The relative reactivities of cis- and trans-1,2,3-trichloro-2-butene and 2,3,3-trichloro-1-butene have been determined for their reaction with potassium iodide in acetone, and with sodium ethoxide in ethanol. Also the relative reactivities of cis- and trans-2,3-dichloro-2-butene for their reaction with sodium ethoxide in ethanol. During the course of preparing some of these compounds, unexpected results were obtained. When 2,3,3-trichloro-1-butene was treated with lithium alumin hydride, only one product was obtained: trans-2,3-dichloro-2-butene. When the same compound was treated with an aqueous solution of sodium carbonate, three products were obtained: cis- and trans-2,3-dichloro-2-butene-1-ol and trans-1,2,3-trichloro-2-butene. The apparent allylic rearrangement with lithium aluminum hydride has not been noted previously.

Within recent years a number of allylic chlorides have been synthesized, their structures determined and their properties studied, especially in respect to the influence of geometrical configuration upon relative reactivity.² Two pairs of

related geometrical isomers which have received particular attention are the crotyl CH chlorides^{2,3} (the 1-chloro-2-butenes) and the 1,3-dichloro-2-butenes.⁴ The present paper reports an extension of this study to include the

1,2,3-trichloro-2-butenes. The diagram illustrates the method used in the preparation of these trichlorides from 1,2,3,3-tetrachlorobutane. The corresponding dichloro alcohols were also prepared from the ethyl α,β,γ -trichlorocrotonates by treatment with lithium aluminum hydride.

In the first method of preparation the 1,2,3,3tetrachlorobutane which was later dehydrochlorinated to give the desired 1,2,3-trichloro-2-butene was prepared by the addition of chlorine to 1,3dichloro-2-butene.⁵ The major product of this reaction was 1,2,3,3-tetrachlorobutane but 2,3,4trichloro-1-butene and 1,2,2,3,4-pentachlorobutane were also formed. It is probable that both the trichloride and the tetrachloride arose from a common intermediate.

This type of reaction mechanism has been proposed to account for the formation of 1,2,3-tri-

(1) Presented in part at the 118th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1950.

(2) For paper number XIII of this series see L. F. Hatch and S. S. Nesbitt, THIS JOURNAL, **73**, 358 (1951).

- (3) L. F. Hatch and S. S. Nesbitt, *ibid.*, 72, 727 (1950).
- (4) L. F. Hatch and S. G. Ballin, ibid., 71, 1039, 1041 (1949).
- (5) W. H. Carothers and G. J. Berchet, ibid., 55, 1628 (1933).

chloro-2-methylpropane and 3-chloro-2-chloromethyl-1-propene, among other compounds, when

(1)
$$CH_{3}CCl = CHCH_{2}Cl + Cl_{2} \rightarrow$$

+ $Cl^{-} \rightarrow$ $CH_{3}CCl_{2}CHClCH_{2}Cl$
 $CH_{3}C^{+}ClCHClCH_{2}Cl -$
 $-H^{+} \rightarrow$ $CH_{2} = CClCHClCH_{2}Cl + HCl$

(II)
$$CH_2 = CClCHClCH_2Cl + Cl_2 -$$

CH₂CIC+CICHCICH₂CI $\xrightarrow{+CI^-}$ CH₂CICCl₂CHCICH₂CI methallyl chloride is treated with chlorine under similar conditions.⁶ Carothers and Berchet⁵ have given a somewhat similar reaction mechanism involving a chlorine–olefin complex to explain the products formed during the chlorination of 1,3dichloro-2-butene. The ratio of addition to substitution in both reaction I (68% addition) and in reaction II (100% addition) is in accord with the generalizations of Taft.⁷

The *trans*-1,2,3-trichloro-2-butene (*trans* in respect to the chlorine atoms on the number 2 and number 3 carbon atoms) obtained by the dehydro-chlorination of 1,2,3,3-tetrachlorobutane was treated with lithium aluminum hydride⁸ and *trans*-2,3-dichloro-2-butene⁹ was the only product. The same trichloride was also hydrolyzed by a sodium carbonate solution to give *trans*-2,3-di-chloro-2-buten-1-ol.

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- (9) D. V. Tishchenko and A. Churbakov, J. Gen. Chem. (U. S. S. R.), 6, 1553 (1936).