

solution 0.75 g. of 2,4-dinitrophenylhydrazine was added and the mixture refluxed for five minutes. Upon cooling the 2,4-dinitrophenylhydrazone separated out (IIIg, IVg), which was recrystallized from alcohol.

2,6-Dimethyl-2,3-cyclohexylcoumarane (V) and 2-Methyl-6-ethyl-2,3-cyclohexylcoumarane (VI).—Half molar quantities of the respective meta-alkylated phenol and *o*-methylcyclohexanone were dissolved in 100 cc. of glacial acetic acid and condensed as described for compound I, except that the reaction was carried out while the reactants were heated on a water-bath to about 80°. The condensation mixture was left standing for fourteen days, but during this time it was resaturated with hydrogen chloride several times. The reaction product was then dissolved in 200 cc. of benzene, this solution washed several times with water and then extracted with 250 cc. of Claisen solution. Upon acidification of the Claisen solution extract only the unreacted *m*-alkylated phenol (*m*-cresol, or *m*-ethylphenol) was recovered. The benzene solution was then subjected to fractional distillation. Compound V boiled at 139–141° and 12 mm.; n_D^{25} 1.5338; sp. gr.²⁵,

1.0252; yield, about 40%. Compound VI boiled at 146–148° and 12 mm.; n_D^{25} 1.5302; sp. gr.²⁵, 1.0218; yield, about 30%.

The authors desire to express their appreciation to Reed and Carnrick, Jersey City, N. J., for the physiological tests performed.

Summary

Steric hindrance phenomena encountered in certain types of ketone-phenol condensation systems were studied.

Cycloalkylene phenols and cycloalkyl coumaranes were isolated in such condensation systems. Of the cycloalkylene phenols which represent new types of unsaturated phenols, numerous derivatives were prepared.

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

The Reaction between Hexabromobenzene and Phenylmagnesium Bromide

BY T. A. GEISSMAN AND R. C. MALLATT

The formation of hexamethyl- and hexaphenylbenzenes in the reaction between hexabromobenzene and methylmagnesium and phenylmagnesium halides was reported by Durand.¹ The identity of the hexamethylbenzene was established by comparison with an authentic sample, but the "hexaphenylbenzene" was later shown to be 1,2,4,5-tetraphenylbenzene by Dilthey,² who prepared this compound by an unambiguous method.

A tentative mechanism for the formation of 1,2,4,5-tetraphenylbenzene was suggested by Dilthey,² which involved first a replacement of four of the six bromine atoms by phenyl groups, followed by a "reduction," yielding 1,4-dimagnesiumbromide-2,3,5,6-tetraphenylbenzene which on hydrolysis would yield the tetraphenylbenzene actually obtained. No experimental evidence was offered to support this proposal other than the observation that metallic magnesium is without action on hexabromobenzene, showing that a simple removal of two bromine atoms, possibly through a free radical intermediate, did not take place.

Since other mechanisms for the formation of

1,2,4,5-tetraphenylbenzene are conceivable it was considered of interest to reexamine the reaction between hexabromobenzene and phenylmagnesium bromide and to isolate (a) intermediates and (b) other products than those mentioned, and to attempt to formulate the reaction upon a factual basis.

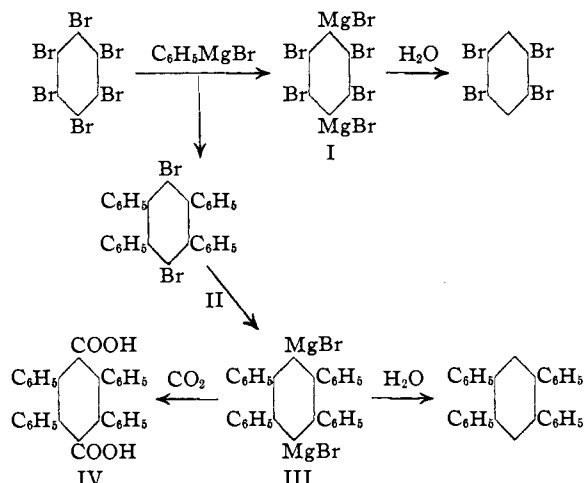
The reaction was carried out in ether, as described by Durand, and a few runs were made in benzene. The chief product of the reaction in either solvent was a dark resinous tar from which the products mentioned below were isolated only with difficulty and in small yields. 1,2,4,5-Tetraphenylbenzene and 1,2,4,5-tetrabromobenzene were obtained by hydrolysis of the reaction mixture, while carbonation led to the formation of 1,2,4,5-tetraphenylbenzene-3,6-dicarboxylic acid (IV). Attempts to show the derivation of the tetrabromobenzene from the postulated intermediate (I) failed to yield tetrabromoterephthalic acid. Similar results were obtained when the solutions of the Grignard reagent were filtered before addition of the hexabromobenzene. This observation, coupled with the fact that an ether-benzene solution of the magnesium-magnesium iodide complex was without effect on hexabromobenzene, leads to the conclusion that reaction be-

(1) Durand, *Compt. rend.*, **191**, 1460 (1930)

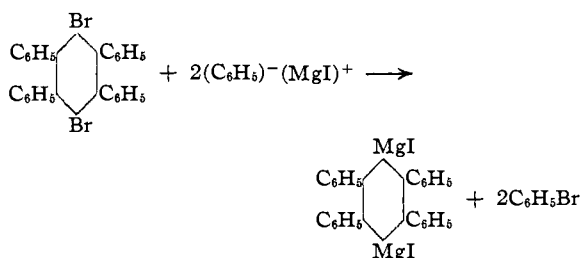
(2) Dilthey, *Ber.*, **67**, 2004 (1934).

tween hexabromobenzene and metallic magnesium or the magnesium-magnesium bromide complex had not occurred.

The results obtained indicate the following course for the reaction



An alternative mechanism in which I is the first intermediate from which III is derived by replacement of the four bromine atoms by phenyl groups cannot explain the formation of hexamethylbenzene when methylmagnesium iodide is used. If this were the mechanism, durene should be formed. In spite of the failure to isolate tetrabromoterephthalic acid by carbonation of the reaction mixture, the above scheme represents the most reasonable picture of the reaction. The reactions leading to I and II are considered to be concurrent and presuppose an amphoteric character in two of the six bromine atoms in hexabromobenzene. The bromine atoms in II, however, as a result of the (-T) effect of the ortho-phenyl groups (in contrast to the effect of ortho-methyl groups) are activated in the same way as the bromine atoms in such compounds as ω -bromoacetomesitylene and diarylbromomethanes and assume a "positive" character. The reaction of hexabromobenzene with phenylmagnesium iodide then involves, as we now find, the additional step



The formation of large amounts of heavy, resinous material in the reaction can be explained by reactions occurring between the intermediates (I and II) and hexabromobenzene. That the use of a large excess of phenylmagnesium bromide nearly doubled the yield of tetraphenylbenzene substantiates this view since the reaction of II with phenylmagnesium bromide to yield III would be speeded up by a large excess of the Grignard reagent. The reaction of hexabromobenzene with phenyllithium led only to highly polymeric solid substances from which no pure substance could be isolated. This follows on the same basis, the more highly reactive lithium intermediates reacting further to form polymeric substances.

The projected study of the reaction between phenylmagnesium bromide and 1,4-dibromo-2,3,5,6-tetraalkyl- and arylbenzenes should throw further light on the mechanism of the reaction.

Experimental

Table I presents a number of representative runs. The reactions were carried out by adding the solid hexabromobenzene to the solution of the Grignard reagent and refluxing the solution for eighteen to twenty-four hours. The hexabromobenzene is practically insoluble in ether but dissolves slowly as the reaction proceeds. Carbonation and hydrolysis of the reaction mixtures were carried out in the usual way.

The products of the reaction were worked up by steam distilling to remove diphenyl, followed by crystallization or distillation under reduced pressure.

TABLE I

C ₆ Br ₆ , g.	Moles C ₆ H ₅ MgBr per mole C ₆ Br ₆	Solvent	C ₆ H ₂ (C ₆ H ₅) ₄ , g.	C ₆ H ₅ Br, g.	Acid, g.
30	8.25	Ether	1.80
10	8.07	Ether	0.50
10	50.90	Ether	1.03
10	8.07	Ether	0.30
10	8.07	Ether	..	0.20	.33
10	8.07	Benzene	..	.40	..
10	8.07	Benzene	..	.50	..
10	8.07	Benzene	..	.90	.30

1,2,4,5-Tetraphenylbenzene.—Distillation of the tarry reaction product under reduced pressure followed by crystallization of the small amount of distillate from acetic acid yielded the hydrocarbon as white needles, m. p. 262–263° (Dilthey² reports melting point of 263°).

Anal. Calcd. for C₃₀H₂₂: C, 94.24; H, 5.76; mol. wt., 378. Found: C, 94.31; H, 5.62; mol. wt. (Rast), 382.

1,2,4,5-Tetrabromobenzene.—The identity of the product was established by a mixed melting point determination with an authentic sample prepared according to the method of van der Linden.³

(3) Van der Linden, *Rec. trav. chim.*, **57**, 781 (1938).

2,3,5,6-Tetraphenylbenzene-1,4-dicarboxylic Acid.—The reaction mixture was carbonated with gaseous carbon dioxide at 0°. After decomposition of the reaction mixture the acidic material was extracted with alkali and precipitated with dilute hydrochloric acid. The resulting solid was boiled with several portions of water to remove benzoic acid and finally crystallized from acetic acid. The acid formed tiny white needles which did not melt up to 320° (bloc Maquenne).

Anal. Calcd. for $C_{32}H_{20}O_4$: C, 81.70; H, 4.70; neut. equiv., 235. Found: C, 81.01; H, 4.71; neut. equiv., 232.

Methyl 2,3,5,6-Tetraphenylbenzene-1,4-dicarboxylate.—The acid was esterified with diazomethane in the usual way. The product crystallized from acetic acid as tiny white prisms, m. p. 280°.

Anal. Calcd. for $C_{34}H_{26}O_4$: C, 81.90; H, 5.40. Found: C, 81.50; H, 5.26.

Phenylmagnesium Iodide and Hexabromobenzene.—To the Grignard reagent prepared from 59.2 g. of iodobenzene and 7.05 g. of magnesium in ether was added 20 g. of

hexabromobenzene. After refluxing for twenty-four hours the reaction mixture was hydrolyzed with ice-hydrochloric acid and steam distilled. Extraction of the distillate with ether followed by distillation yielded 3.20 g. of bromobenzene, identified by its boiling point and by the preparation of *p*-nitrobromobenzene, m. p. 127–128°; mixed with an authentic sample, m. p. 126–128°. The residue from the steam distillation yielded 0.90 g. (7.9%) of 1,2,4,5-tetraphenylbenzene, m. p. 260–262°.

Summary

1. The reaction between hexabromobenzene and phenylmagnesium bromide has been reinvestigated, and the intermediate formation of 2,3,5,6-tetraphenylbenzene-1,4-dimagnesium bromide has been established.

2. An explanation of the course of the reaction has been suggested.

URBANA, ILLINOIS

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[CONTRIBUTION NO. 160 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

Tertiary Alkyl Primary Amines, $RR'R''CNH_2$. I. Ethoxymethyldiallylcarbinamine and Some Analogs^{1,2}

BY BRUCE B. ALLEN AND HENRY R. HENZE

There has been in progress in this Laboratory for some years an extensive study of substituted ketones of the alkoxy, aryloxy, and halogenoalkoxy alkyl (and aryl) types. Such ketones have been and are being synthesized from the appropriate substituted nitriles by means of Béhal and Sommelet's³ modification of the Grignard reaction; with the exception of the tertiary butyl analogs, relatively little difficulty has been experienced in obtaining, for almost every series, both the straight and branched chain alkyl derivatives through the amyls. Since these numerous ketones have been synthesized with the view to their further use in the preparation of compounds having physiological activity, it became desirable to have examples in which the alkoxy alkenyl grouping was represented. Hence, an attempt was made to prepare ethoxymethyl allyl ketone from ethoxyacetonitrile and allylmagnesium bromide.

It was noted with considerable surprise, then, that when equimolecular quantities of allylmagnesium bromide, prepared independently accord-

ing to Gilman,⁴ and ethoxyacetonitrile were brought together, apparently only one-half of the nitrile reacted, and although a constant boiling product was obtained, no ketonic material was formed. Moreover, this product, while possessing physical constants which made impossible its being unreacted nitrile, contained nitrogen, was basic in character, formed solid derivatives with such common amine reagents as picric acid and phenyl isocyanate, but failed to undergo the typical primary amine reaction of isonitrile formation. In a subsequent preparation it was found that by increasing the ratio of Grignard reagent to nitrile from 1:1 to 2:1 no unreacted nitrile was recovered and a correspondingly greater yield of basic product was formed.

Analyses of the purified, basic substance established $C_{10}H_{19}NO$ as its empirical formula. It was possible to conceive of the addition of two molecules of allylmagnesium bromide to one of ethoxyacetonitrile and of subsequent hydrolysis of the addition product to yield a compound of molecular formula $C_{10}H_{19}NO$. Analysis of the picrate of the basic compound obtained verified this formulation.

(1) Presented before the Division of Organic Chemistry at the 97th meeting of the American Chemical Society at Baltimore, Maryland, April 3–7, 1939.

(2) From the Ph.D. dissertation of B. B. Allen, June, 1938.

(3) Béhal and Sommelet, *Compt. rend.*, **138**, 89 (1904).

(4) Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).