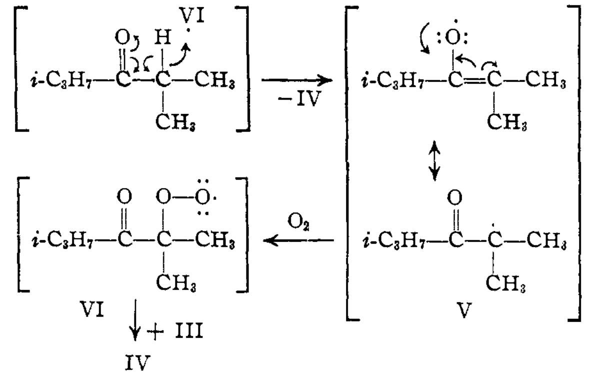
mechanism is proposed as a possible chain propagation step for the formation of the hydroperoxide.



Simple decomposition of IV into acetone and isobutyric acid can be written in a stoichiometric equation, but the appreciable production of water suggests a more involved decomposition sequence to give the final products. Studies of the kinetics of this oxidation are continuing and will be the subject of a future communication.

The infrared absorption spectra in Fig. 4 show a marked increase in absorption after 32 hours at a wave length of about 2.9 μ. Absorption in this wave length region has been designated[24] as being due to O–H stretching and the absorption at about 3.4 μ has been assigned[24] to C–H stretching. The increase of optical density at 2.9 μ with increased oxidation time indicates the development of hydroxyl groups in the form of the hydroperoxide, isobutyric acid or water or any combination of the three. The strong absorption at this region obtained with the pure hydroperoxide is confirmatory evidence for the existence of the hydroperoxy group in that molecule.

Acknowledgment.—The authors are indebted to Mr. A. Dwight Moorhead and Mr. B. L. Thompson for assistance in obtaining the spectroscopic data, and to the Office of Naval Research under whose sponsorship this investigation was conducted. We also gratefully acknowledge the aid in interpretation of the kinetic data given by Dr. M. K. Testerman and Dr. J. L. Hall of the Department of Chemistry.

[24] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Company, New York, N. Y., 1949, p. 43.

MANHATTAN, KANSAS RECEIVED OCTOBER 16, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND]

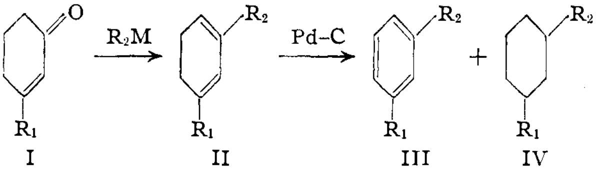
Synthesis of *m*-Dialkylbenzenes

BY G. FORREST WOODS AND ROBERT E. PLAPINGER

A number of *m*-dialkylbenzenes were prepared from 3-alkyl-Δ^2-cyclohexenones by means of the Grignard reaction followed by dehydrogenation over palladium-charcoal. Purification of the aromatic products was accomplished by sulfonation, extraction of the non-aromatic by-products and hydrolysis of the sulfonic acids.

A general method of synthesis of *m*-dialkylbenzenes has long been needed. The best approach to such a preparation has been the use of the Wurtz–Fittig or the Friedel–Crafts reaction. The former has not been useful because of the unavailability of the various *m*-haloalkylbenzenes. The numerous difficulties of the Friedel–Crafts reaction in this type of synthesis are too well known to merit mention here.

Recent publications[1] from this Laboratory have described the preparation of 3-alkyl-Δ^2-cyclohexenones from dihydroresorcinol monoethyl ether. This paper is a report on the utilization of these substances in the preparation of *m*-dialkylbenzenes. The reactions used are shown in Equation 1



The usual difficulties were encountered in the first stage of the reaction; for example, the reaction between *t*-butylmagnesium chloride and 3-*n*-butyl-Δ^2-cyclohexenone afforded none of the desired diene. Presumably the Grignard reagent reacted with the enolic form of the ketone since the ketone was recovered almost completely. However, the expected bond isomer was obtained by addition of *n*-butylmagnesium bromide to 3-*t*-butyl-Δ^2-cyclohexenone.

Table I lists the physical and analytical data for the 1,3-dialkylcyclohexadienes-1,3 (II) obtained in the course of this study.

Unlike 1,3-diarylcyclohexadienes[2] which are readily aromatized over palladium–charcoal catalyst, the 1,3-dialkylcyclohexadienes-1,3 (II) underwent severe disproportionation to yield, in addition to the benzenoid compound (III), 1,3-dialkylcyclohexane (IV).

The purification or separation of these two substances was accomplished in the following manner. The aromatic compound was sulfonated in the cold with concentrated sulfuric acid. After dilution with water, the mixture was extracted with pentane. The aromatic compound was recovered by hydrolysis of the sulfonic acid group and the dialkylcyclohexane could be recovered by fractional distillation of the pentane layer.

It was found that when a 60% sulfuric acid

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[1] G. F. Woods, P. H. Griswold, B. H. Armbrecht, D. I. Blumenthal and R. E. Plapinger, THIS JOURNAL, **71**, 2028 (1949).

[2] (a) G. F. Woods and I. W. Tucker, *ibid.*, **70**, 2174 (1948); (b) *ibid.*, **70**, 3340 (1948); (c) G. F. Woods and F. T. Reed, *ibid.*, **71**, 1348 (1949); (d) G. F. Woods, A. L. Van Artsdale and F. T. Reed, *ibid.*, **72**, 3221 (1950).

TABLE I

1,3-DIALKYLCYCLOHEXADIENES-1,3

	Yield, %	B.p.			Analyses, %			
					Calcd.		Found	
		°C.	Mm.	$n^{25}D$	C	H	C	H
$R_1 = R_2 = CH_3$	67[b]	54	34[a]	1.4850[a]	88.91	11.09	88.92	11.26
	68[c]	138	760				88.89	11.27
$R_1 = R_2 = C_2H_5$	69	76–78	16	1.4995	88.17	11.83	88.31	12.10
$R_1 = n\text{-}C_4H_9$	83	105–106	15	1.4958	87.73	12.27	87.59	12.21
$R_2 = C_2H_5$								
$R_1 = R_2 = C_4H_9$	80	84	1.8	1.4882	87.42	12.58	87.31	12.75
$R_1 = t\text{-}C_4H_9$	84	65–66	0.4	1.4823	87.42	12.58	87.07	12.52
$R_2 = n\text{-}C_4H_9$								

[a] W. N. Haworth, *J. Chem. Soc.*, **103**, 1244 (1913), reported a b.p. of 135° and $n^{20}D$ 1.4853 for this compound. [b] Methylmagnesium bromide. [c] Methyllithium.

TABLE II

	Yield, %	B.p.			Analyses, %			
					Calcd.		Found	
		°C.	Mm.	$n^{25}D$	C	H	C	H
m-Xylene	29	61	43	1.4951	90.51	9.49	90.62	9.83
		139	760					
$R_1 = R_2 = C_2H_5$[a]	24	65	12	1.4935	89.49	10.51	89.52	10.54
		181	760					
$R_1 = C_2H_5$	56	104	16	1.4892	88.82	11.18	88.77	11.22
$R_2 = n\text{-}C_4H_9$		221	760					
$R_1 = R_2 = n\text{-}C_4H_9$	60	75–76	0.4	1.4860	88.34	11.66	88.34	11.42
		254–255	760					
$R_1 = t\text{-}C_4H_9$	20	66	0.8	1.4878	88.34	11.66	88.64	11.60
$R_2 = n\text{-}C_4H_9$		240	760					

[a] J. E. Copenhaver and E. E. Reid, THIS JOURNAL, **49**, 3160 (1927), reported a boiling point of 180.55°, and $n^{25}D$ of 1.4926 for this compound.

solution containing sulfonated *m*-di-*n*-butylbenzene was extracted with low boiling petroleum ether, the sulfonic acid passed into the organic layer from which it was obtained as a red oil which could be crystallized from higher boiling petroleum ether to give, after clarification, white crystals which were soluble in ether, benzene and warm cyclohexene, in addition to alcohol and water. No attempt was undertaken to determine the structure of this substance. Analysis indicated that the crystalline sulfonic acid was a monohydrate.

Five hydrocarbons were prepared by the aromatization procedure, and the physical and analytical data are recorded in Table II.

The "yields" column represents the over-all yields of the three steps from II to the purified aromatic compounds. The structure of four of these compounds was established by oxidation to isophthalic acid and *m*-*n*-butyl-*t*-butylbenzene was identified by oxidation to *m*-*t*-butylbenzoic acid.

Ultraviolet absorption spectra were obtained for the five benzenoid hydrocarbons; the spectrum of *m*-xylene and *m*-diethylbenzene are essentially identical with the corresponding spectra given in the reports of the American Petroleum Institute Project Number 44. The other three spectra were very similar to that of *m*-diethylbenzene.

A sample of 1-ethyl-3-*n*-butylcyclohexane was obtained from the pentane layer used in extracting the water solution of sulfonated *m*-ethyl-*n*-butylbenzene.

Experimental

Preparation of 1,3-Dialkylcyclohexadienes-1,3.—These compounds were all obtained by essentially the same procedure. The appropriate Grignard reagent in ether was prepared in 50% excess by standard methods. The 3-alkyl-cyclohexenone in about five times its volume of ether was added with stirring. The Grignard addition complex was decomposed with a 10% sulfuric acid solution. The ether layer was shaken with dilute sodium bicarbonate solution and dried over magnesium sulfate. The dienes (II) were isolated by vacuum distillation of the ether layer. The dienes isolated in this manner were contaminated with slight traces of tertiary alcohol. To obtain a sample of cyclohexadiene (II) suitable for analysis the tertiary alcohol was removed by either steam distillation of the diene from 5–10% sulfuric acid solution followed by extraction and distillation or by chromatographic adsorption on alumina of the alcohol from a petroleum ether solution of the crude diene. The latter method involved smaller losses of material but the former was far more effective. The yields, physical properties and analytical data for these substances are given in Table I. In actual practice, a small portion of the cyclohexadiene (II) was purified while the bulk containing traces of tertiary alcohol was used for the subsequent steps as slight traces of carbinol would yield the same dehydrogenation product as the diene with palladium on charcoal catalyst.

The 1,3-dialkylcyclohexadienes-1,3 were all clear colorless liquids with very pleasant odors, unstable with polymerization if maintained at room temperature but stable indefinitely if stored in a refrigerator.

Preparation of *m*-Dialkylbenzenes.—The dialkylcyclohexadienes (II) were all aromatized in the same fashion. The diene was added dropwise through a heated tube (120°) onto approximately 10% of its weight of 10% palladium on charcoal catalyst in a small boiling flask. This flask was immersed in a hot (200°) oil-bath during the addition of the diene. The temperature of the oil-bath was progressively increased as the molecular weight of the diene increased. After all the diene had been added, the mixture was refluxed over the palladium-on-charcoal catalyst for a four-hour period. On cooling, the catalyst was removed by filtration and rinsed with ether. The ethereal solution was dried and distilled under reduced pressure. The dehydrogenation product in all cases distilled over a fairly constant boiling range as a colorless, homogeneous liquid. Carbon and hydrogen analysis, sulfonation and oxidation experiments established that this liquid was a mixture of dialkylbenzene and dialkylcyclohexane. To effect a separation of the aromatic compound from the alicyclic by-product the distillate in each case was added to an excess of concentrated sulfuric acid with stirring, the temperature of the sulfuric acid mixture being maintained at 15°. After the addition was complete, stirring was continued for 16 hours at room temperature. This mixture was poured into an equal volume of water (cracked ice).

In the case of *m*-xylene and *m*-diethylbenzene this diluted medium was extracted several times with *n*-pentane. The sulfuric acid layer was then subjected to steam distillation yielding the desired hydrocarbon.

In the case of *m*-ethyl-*n*-butylbenzene and *m*-*n*-butyl-*t*-butylbenzene the original sulfonation mixture (containing sulfuric acid of sp. gr. 1.84) was diluted with an equal volume of water. The red oil which formed on top of the sulfuric acid layer was separated and diluted with about ten times its volume of water. This solution was extracted several times with *n*-pentane. The sulfonic acid was rendered insoluble by addition of concentrated sulfuric acid to the water and the organic layer was then subjected to steam distillation yielding the desired hydrocarbon.

When the sulfuric acid medium (sp. gr. 1.84) containing sulfonated *m*-di-*n*-butylbenzene was diluted 1 to 1 with water and extracted with low boiling petroleum ether, the sulfonic acid was found in the petroleum ether layer. On evaporation of the petroleum ether the acid was obtained as a red oil which upon crystallization from 30–60° petroleum ether gave pinkish white crystals which melted at 58–61°. This solid was soluble in ether, benzene, hot cyclohexane, in addition to water and alcohol. Clarification with carbon and recrystallization from 60–80° petroleum ether gave white crystals which melted at 62–64°.

Anal. Calcd. for $C_{14}H_{22}SO_3 \cdot H_2O$: C, 58.29; H, 8.38. Found: C, 58,19; H, 8.51.

After steam distillation the benzenoid hydrocarbons in every case were obtained by extraction of the steam distillate with ether, drying and distillation. The yields, physical properties and analytical data for these hydrocarbons can be found in Table I.

m-Xylene, *m*-diethylbenzene, *m*-ethyl-*n*-butylbenzene and *m*-di-*n*-butylbenzene were all oxidized with alkaline permanganate to isophthalic acid. The white solids obtained on oxidation melted above 300°. A mixed melting point determination with an authentic sample of isophthalic acid in every case melted above 300°. The di-(*p*-bromophenacyl) ester derivative of this acid was prepared in every case. These derivatives melted at 185° and gave no depression in a mixed melting point determination with the derivative prepared from an authentic sample of isophthalic acid.

2,4,6-Trinitro-*m*-xylene was prepared from our *m*-xylene sample. It melted at 182° and showed no depression in a mixed melting point determination with the 2,4,6-trinitro-derivative prepared from an authentic sample of *m*-xylene.

Preparation of *m*-*t*-Butylbenzoic Acid.—*m*-*n*-Butyl-*t*-butylbenzene (2.0 g.) was placed in 100 ml. of water in a three-neck 300-ml. flask with stirrer and reflux condenser attached. Potassium permanganate (4.0 g.) was added over a 24-hour period. The manganese dioxide was filtered and the excess potassium permanganate destroyed and then acidified with concentrated hydrochloric acid. White needles formed which on recrystallization from aqueous alcohol melted at 127° in agreement with earlier reports.[3]

Isolation of 1-Ethyl-3-*n*-butylcyclohexane.—The pentane layer which had been used to extract the solution containing sulfonated *m*-ethyl-*n*-butylbenzene was dried and then subjected to fractional distillation. After removal of the pentane a colorless liquid, 17 g. (from 82 g. of diene) was isolated, b.p. 98° (17 mm.). Redistillation of this material yielded 1-ethyl-3-*n*-butylcyclohexane, $n^{25}D$ 1.4442.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.63; H, 14.37. Found: C, 85.71; H, 14.43.

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(3) K. T. Serijan, H. F. Hipsher and L. C. Gibbons, THIS JOURNAL, **71**, 1873 (1949).

COLLEGE PARK, MARYLAND

RECEIVED MAY 12, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

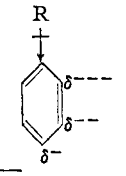
Distribution of Isomers in the Mononitration of *t*-Butylbenzene; Properties of the Pure Mononitro-*t*-butylbenzenes

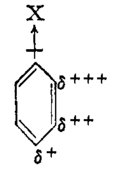
BY K. LEROI NELSON[1] AND HERBERT C. BROWN

Nitration of *t*-butylbenzene with mixed acid yields *o*-, *m*- and *p*-nitro-*t*-butylbenzene in proportions of 15.8:11.5:72.7, respectively. The ortho/meta ratio is 1.37 as compared with 13.3 for toluene. The para/meta ratio is 6.32 as compared with 8.45 for toluene. The marked decrease in ortho substitution is attributed to the steric effect of the bulky *t*-butyl group. The individual mononitro-*t*-butylbenzenes have been carefully purified and their physical properties determined.

Discussion

Orientation in the substitution of benzene derivatives has been the subject of a wide variety of investigations from which a number of simplifying principles have emerged. Current theory has concerned itself primarily with the importance of electrical factors in controlling substitution. Thus, attempts have been made to correlate the observed ortho/para ratios in aromatic substitution with these electrical factors. According to this interpretation, inductive effects will activate the various ring positions in an inverse proportion to the distance from the substituent.[2]





However, it has not been possible to account for the observed ortho/para ratios in aromatic substitution in terms of the electrical factor alone. Certain anomalies in these ratios were attributed by LeFevre and his co-workers to steric hindrance by large substituent groups.[3] In this way the probability of ortho substitution would be dependent upon both the steric requirements and the electrical characteristics of the substituent groups. In support of his proposal LeFevre pointed out that electrophilic substitution of 1-methyl-4-isopropylbenzene occurs preponderantly at the 2-position.[3] However, it was pointed out that the results do not necessarily support the proposed interpretation in terms of steric effects. Consideration of hyperconjugation possibilities suggests that the position ortho to the methyl group should be more suscep-

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(1) A. E. C. Fellow at Purdue University, 1950–1951.

(2) A. Lapworth and R. Robinson, *Mem. Proc. Manchester Lit. & Phil. Soc.*, **72**, 43 (1927).

(3) (a) R. J. W. LeFevre, *J. Chem. Soc.*, 977, 980 (1933); 1501 (1934); (b) S. N. Ganguly and R. J. W. LeFevre, *ibid.*, 848, 852 (1934). For more recent discussion of steric effects as a factor in ortho substitution, see P. B. D. de la Mare and P. W. Robertson, *ibid.*, 279 (1943); E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949); M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949), and P. B. D. de la Mare, *ibid.*, 2871 (1949).