tion of the organic layer gave 133 g. of unreacted mesityl oxide, and 396 g. (80%) of β,δ-dimethyl-$\Delta^{\beta,\gamma}$-δ-hexenolactone (VIII) b. p. 92–93° (2 mm.); sp. gr. $^{20}_{15.6}$ 1.012; n^{30}_D 1.4600. *Anal.* Calcd. for $C_8H_{12}O_2$: C, 68.6; H, 8.6; sapn. equiv., 140.3. Found: C, 68.5; H, 8.5; sapn. equiv., 140.0.

β,δ-Dimethylsorbic Acid.—Fifty grams of VIII was refluxed eight hours with 100 ml. of 50% sodium hydroxide solution. The clear solution was cooled to 10° and strongly acidified. β,δ-Dimethylsorbic acid crystallized and was filtered off (24 g., 48%), m. p. 94–95°, undepressed by admixture with authentic material. By extraction of the filtrate with ether 25 g. of reformed VIII was isolated.

β-Methyl-$\Delta^{\beta,\gamma}$-δ-octenolactone (IX).—One hundred and nine grams of ketene was introduced at 10° into a solution of 291 g. of butylidene acetone dissolved in 800 ml. of ether containing 4 g. of boron trifluoride. The catalyst was destroyed with sodium hydroxide as previously described. Distillation gave 73 g. unreacted ketone and 298 g. (99%) of IX, b. p. 111° (3.5 mm.); sp. gr. $^{20}_{15.6}$ 1.002; n^{30}_D 1.4660. *Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.0; H, 9.2; sapn. equiv., 154.2. Found: C, 70.1; H, 9.2; sapn. equiv., 154.2.

Summary

β,γ-Unsaturated δ-lactones were readily obtained by the reaction of ketene with β-alkyl vinyl methyl ketones in the presence of boron trifluoride.

The β,γ-unsaturated lactones were transformed quantitatively to α,β-unsaturated lactones by heating with potassium carbonate.

The mechanism for the condensation reaction is discussed.

South Charleston, West Virginia

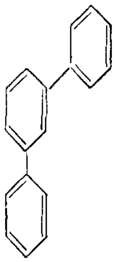
Received October 20, 1948

[Contribution from the Chemical Laboratories of The University of Maryland]

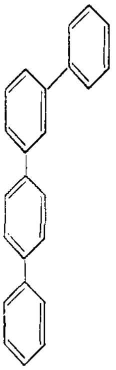
m-Diarylbenzenes

By G. Forrest Woods and Fred T. Reed

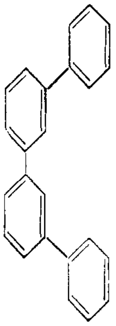
The reaction of the monoethyl ether of dihydroresorcinol with organo-metallic reagents[1] gives rise to a series of *m*-diarylbenzenes.



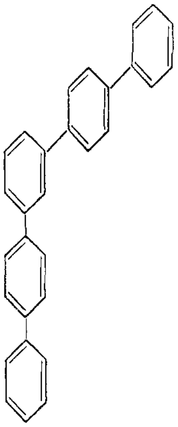
V



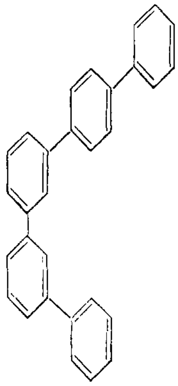
VI



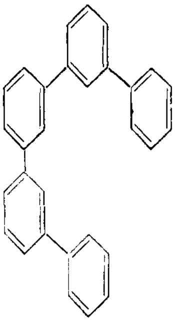
VII



VIII



IX



X

An earlier communication[2] described the preparation of V, VI and VIII. The present study describes the preparation of VII, IX and X, these syntheses being summarized in the flow sheet.

The intermediate dienes were not isolated and identified in all cases, since they undergo oxidation very readily, presumably to the aromatic compounds. In practice, the dienes were treated directly without purification with palladium–charcoal to effect aromatization. 1-Phenyl-3-(3-xenyl)-benzene, VII, was best prepared by the reaction of IV with 3-xenylmagnesium bromide rather than by the alternate route since a Wurtz type of reaction in the preparation of 3-xenylmagnesium bromide gives VII as a product. Substance VII, obtained by either procedure, corresponds in properties with those reported by Bowden[3] for 1-phenyl-3-(3-xenyl)-benzene prepared by the treatment of 3-xenyl iodide with copper powder. Substance IX was best prepared by treating II with 3-xenylmagnesium bromide rather than by the alternate method. Substance X could be prepared only by the one series of reactions indicated.

The authors wish to acknowledge that this work was supported in part by a contract from the Office of Naval Research.

Experimental

Preparation of 3-Xenyl Bromide.—The synthesis of 3-xenyl bromide, first attempted without success by the Gomberg–Bachmann[4] reaction, was realized by the method of Huber, *et al.*,[5] modified by extracting the deamination reaction mixture with ether and obtaining crude 3-xenyl bromide by distillation of this extract. A solution prepared by adding an approximately equal volume of 30–60° petroleum ether to the crude 3-xenyl bromide was passed through a chromatographic column packed with activated alumina, resulting in an effective removal of colored impurities. The resulting solution was distilled, yielding

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(1) Woods and Tucker, This Journal, **70**, 2174 (1948).

(2) Woods and Tucker, *ibid.*, **70**, 3340 (1948).

(3) Bowden, *J. Chem. Soc.*, **139**, 111 (1931).

(4) Gomberg and Bachmann, This Journal, **46**, 2339 (1924).

(5) Huber, *et al.*, *ibid.*, **68**, 1111 (1946).

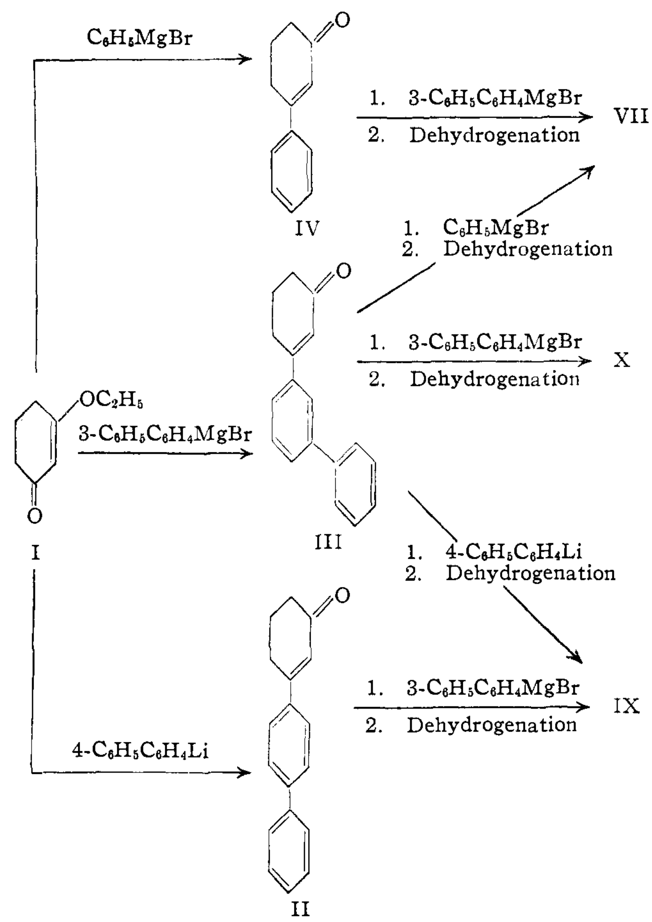

CHART I

water white 3-xenyl bromide boiling at 113–115° at 0.1 mm. Physical constants agreed with those reported by Huber, *et al.*, and yields were about the same.

Since this work dealt in part with positional isomerism, the identity of the above product was determined as follows: Fifteen grams of the 3-xenyl bromide was converted to the Grignard reagent by reaction with 1.6 g. of magnesium in 35 ml. of dry ether. This was poured into a mixture of dry ice and ether and then acidified with 150 ml. of 10% sulfuric acid. After washing the ether layer with 20% sulfuric acid, it was extracted with a 25% solution of potassium hydroxide. Acidification of the alkaline extract gave 9 g. of crude 3-xenylcarboxylic acid, melting at 150–3°, a 70% yield.

Preparation of 1-Phenyl-3-(3-xenyl)-benzene (VII).—(A) A solution of 92 g. of monoethyl ether of dihydroresorcinol[1] (I) in dry ether (100 ml.) was added to a solution of 3-xenylmagnesium bromide prepared from 3-xenyl bromide (142.6 g.) and magnesium (14.8 g.) in dry ether (250 ml.) in the usual manner. The resulting mixture was hydrolyzed with 10% sulfuric acid (about 100 ml.) and steam-distilled until no organic material was observed in the distillate. The residue was extracted with ether, washed with sodium bicarbonate solution and with water, and dried over magnesium sulfate. After removal of solvent the residue was distilled in a Hickman apparatus using a high vacuum diffusion pump. An extremely viscous, slightly colored distillate (70 g.) of 3-(3-xenyl)-Δ^2-cyclohexenone (III) was obtained. Attempts to crystallize this compound were without success.

The red 2,4-dinitrophenylhydrazone of this compound was prepared, m. p. 210–211°. *Anal.* Calcd. for $C_{24}H_{20}O_4N_4$: C, 67.28; H, 4.71. Found: C, 67.81; H, 4.68.

The intermediate compound 1-(3-xenyl)-3-phenylcyclohexediene-1,3 was prepared by the addition of 3-(3-xenyl)-Δ^2-cyclohexenone (III) (25 g.) in dry ether (20 ml.) to a solution (40 ml.) of phenylmagnesium bromide prepared from bromobenzene (25 g.) and magnesium (3.3 g.) in the usual manner. The resulting mixture was hydrolyzed with 10% sulfuric acid (about 50 ml.) and the impurities removed in part by steam-distillation. The gummy residue, washed several times by water using decantation, was extracted with ether, and dried over magnesium sulfate. After removal of the solvent, the residue was distilled in the Hickman apparatus as before. 1-(3-Xenyl)-3-phenylcyclohexediene-1,3 (22.7 g.), a highly viscous substance was obtained, which did not crystallize.

This substance (7.7 g.) was dehydrogenated[1] by treatment with 5% palladinized charcoal (4 g.) in refluxing *p*-cymene (25 ml.) for three hours. Most of the cymene was removed by distillation and to the residue was added 100 ml. of ethyl alcohol. The catalyst was removed by filtration of the hot solution. Cooling of the filtrate yielded 3.43 g. of 1-phenyl-3-(3-xenyl)-benzene (VII) which melted at 85.5–86.0°[6] after recrystallization from ethyl alcohol. *Anal.* Calcd. for $C_{24}H_{18}$: C, 94.07; H, 5.91. Found: C, 93.63; H, 6.05.

(B) Employing the method of Woods and Tucker,[1] 3-phenyl-Δ^2-cyclohexenone (IV) was prepared.

A solution of this substance (9.7 g.) in dry ether (30 ml.) was added to 40 ml. of dry ether solution of 3-xenylmagnesium bromide prepared from 3-xenyl bromide (16.3 g.) and magnesium (1.58 g.). The Grignard complex thus formed was isolated by rapid filtration and then hydrolyzed with 10% sulfuric acid. The mixture obtained was extracted with ether and the extract washed with sodium bicarbonate solution and with water and dried over magnesium sulfate. After filtration, the ether was permitted to evaporate and there remained a viscous residue composed principally of 1-phenyl-3-(3-xenyl)-cyclohexadiene-1,3. No further attempt at isolation or purification was made.

A portion of this material (about 2 g.) was aromatized and the product (about 1 g.) isolated exactly as described in (A). The 1-phenyl-3-(3-xenyl)-benzene (VII) thus obtained melted at 84.5–85.0° and showed no depression in melting point when mixed with an equal portion of the product obtained by procedure (A).

Preparation of 1-(4-xenyl)-3-(3-xenyl)-benzene (IX).—(A) 3-(4-Xenyl)-Δ^2-cyclohexenone (II) was prepared as described by Woods and Tucker.[2]

To a solution of 3-xenylmagnesium bromide, prepared from 3-xenyl bromide (25 g.) and magnesium (2 g.) in dry ether (40 ml.), was added 3-(4-xenyl)-Δ^2-cyclohexenone (II) (15.0 g.) as finely divided solid. After the reaction was complete, the reaction vessel was chilled in a salt–ice bath to precipitate the Grignard complex. The complex was isolated by filtration and hydrolyzed with cold 10% sulfuric acid (about 50 ml.). The hydrolysis mixture was extracted with benzene and the solution washed with water and sodium bicarbonate solution and finally dried over magnesium sulfate. After removal of a portion of the benzene, a precipitate was obtained upon chilling. Recrystallization of this solid from ethyl alcohol yielded 1-(4-xenyl)-3-(3-xenyl)-cyclohexadiene-1,3 (9.6 g.), melting at 148–149°. *Anal.* Calcd. for $C_{30}H_{24}$: C, 93.70; H, 6.29. Found: C, 93.35; H, 6.48.

This compound (2.4 g.) was dehydrogenated by the same procedure as before using *p*-cymene (25 ml.) and 5% palladinized charcoal (0.5 g.). Benzene was added to the dehydrogenation mixture and the catalyst removed by filtration. Upon addition of an equal volume of ethyl alcohol crystals of 1-(4-xenyl)-3-(3-xenyl)-benzene (IX)

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(6) Bowden reports a melting point of 86° for this compound (*cf.* ref. 3).

(1.89 g.) were obtained. These were recrystallized from an equal mixture of benzene and alcohol, m. p. 155.0–155.5°. *Anal.* Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.57; H, 5.67.

(B) 3-(3-Xenyl)-Δ^2-cyclohexenone (III) was prepared as described above.

A 40-ml. dry ether solution of the substance (17.6 g.) was added to a 40-ml. dry ether solution of 4-xenyllithium, prepared from 4-xenyl bromide (35.0 g.) and lithium (0.76 g.). Hydrolysis of the complex formed was effected as before with 10% sulfuric acid (50 ml.) and the resulting mixture was steam-distilled until there was no further appearance of organic material in the distillate. The residue was extracted with benzene, the extract being then washed successively with sodium bicarbonate solution and with water and finally dried over magnesium sulfate. This was filtered and the solvent allowed to evaporate. The resulting residue of 1-(3-xenyl)-3-(4-xenyl)-cyclohexediene-1,3 was not purified further.

This crude product (3.60 g.) was aromatized as described in procedure A, and the residue taken up in benzene. After filtration and addition of about four times the volume of ethyl alcohol, crystals of 1-(4-xenyl)-3-(3-xenyl)-benzene (IX) were obtained which upon recrystallization from an equal mixture of benzene and ethyl alcohol melted at 153–154°. Mixed melting point with the product obtained by procedure A showed no depression.

Preparation of 1,3-Di-(3-xenyl)-benzene (X).—A Grignard solution prepared in dry ether (40 ml.) from 3-xenyl bromide (30.3 g.) and magnesium (3.2 g.) was treated with a dry ether solution (20 ml.) of 3-(3-xenyl)-Δ^2-cyclohexenone (III). The Grignard complex was isolated as before by rapid filtration of the chilled ether reaction mixture. The precipitate obtained was hydrolyzed with cold 10% sulfuric acid and then extracted with ether. The extract was washed with water and sodium bicarbonate solution and dried over magnesium sulfate. After removal of the solvent, distillation of the residue in the Hickmann apparatus yielded a very viscous yellow liquid (11.36 g.). Attempts to crystallize this material were unsuccessful.

Dehydrogenation of this substance was accomplished as before, by adding dropwise the 1,3-di-(3-xenyl)-cyclohexediene-1,3 (7.55 g.) to a refluxing mixture of 5% palladinized charcoal (4 g.) in *p*-cymene (25 ml.). The reaction mixture was worked up as before using ethyl alcohol, but crystallization from this solution yielded an oil. A portion of this oil was dissolved in benzene–petroleum ether (30–60°) and, upon cooling, crystalline material precipitated, which upon recrystallization from benzene and petroleum ether, yielded 1,3-di-(3-xenyl)-benzene, melting at 97–98°. *Anal.* Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.60; H, 5.89.

Summary

The reaction of the monoethyl ether of dihydroresorcinol with organo-metallic reagents has been extended to include the preparation of 1-phenyl-3-(3-xenyl)-benzene, 1-(4-xenyl)-3-(3-xenyl)-benzene and 1,3-di-(3-xenyl)-benzene.

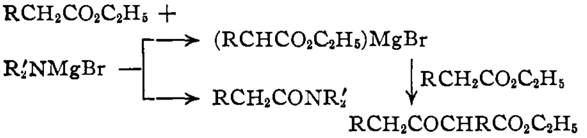
COLLEGE PARK, MD. RECEIVED SEPTEMBER 23, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Condensations of Esters by Diisopropylaminomagnesium Bromide and Certain Related Reagents[1]

BY FREDERICK C. FROSTICK, JR., AND CHARLES R. HAUSER

Dialkylaminomagnesium bromides may react with esters either at the α-hydrogen, effecting their condensations, or at the carbonyl carbon to form the corresponding N,N-dialkylamide, thus



$$\mathrm{RCH_2CO_2C_2H_5} + \mathrm{R'_2NMgBr} \begin{cases} \longrightarrow \mathrm{(RCHCO_2C_2H_5)MgBr} \xrightarrow{\mathrm{RCH_2CO_2C_2H_5}} \mathrm{RCH_2COCHRCO_2C_2H_5} \\ \longrightarrow \mathrm{RCH_2CONR'_2} \end{cases}$$

Diethylaminomagnesium bromide has recently been shown[2] to effect the self-condensation of ethyl phenylacetate, *t*-butyl acetate and certain other esters but not ethyl *i*-valerate and ethyl *i*-butyrate with which the amide is presumably formed. This reagent self-condensed ethyl *n*-butyrate, but the condensation product was contaminated with the amide. The condensation product from ethyl propionate was reported free of the amide, but later work has shown that this condensation product also is generally contaminated with the amide.[3]

In the present investigation, diisopropylaminomagnesium bromide has been found to be a more suitable condensing agent than diethylaminomagnesium bromide. The diisopropyl reagent effects in good yield the self-condensation not only of the straight chain esters, ethyl propionate, ethyl *n*-butyrate and methyl laurate, but also that of the branched chain esters, ethyl *i*-valerate and ethyl *i*-butyrate, which are known to be more difficult to condense. The results are summarized in Table I. The yields have been based on the diisopropylaminomagnesium bromide since a 10% excess of the ester was employed; however, the yields would be approximately the same if they were based on the ester used minus that recovered. The condensation products were shown by the sodium fusion test for nitrogen to be free from the amide with the exception of that from ethyl *i*-valerate when the reaction time was twenty hours; in this case, secondary reactions appeared to have occurred. The products obtained when the reac-

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[1] Paper XLII on "Condensations"; paper XLIII, THIS JOURNAL, **71**, 770 (1949).

[2] Hauser and Walker, *ibid.*, **69**, 295 (1947).

[3] In a private communication, Dr. Robert W. Holley of the State College of Washington, Pullman, Washington, has stated that the condensation product he obtained from ethyl propionate using diethylaminomagnesium bromide was contaminated with the amide. We have similarly found that this condensation product is contaminated with the amide (as detected by the sodium fusion test) when the reaction is carried out for either one-half hour or for four hours.