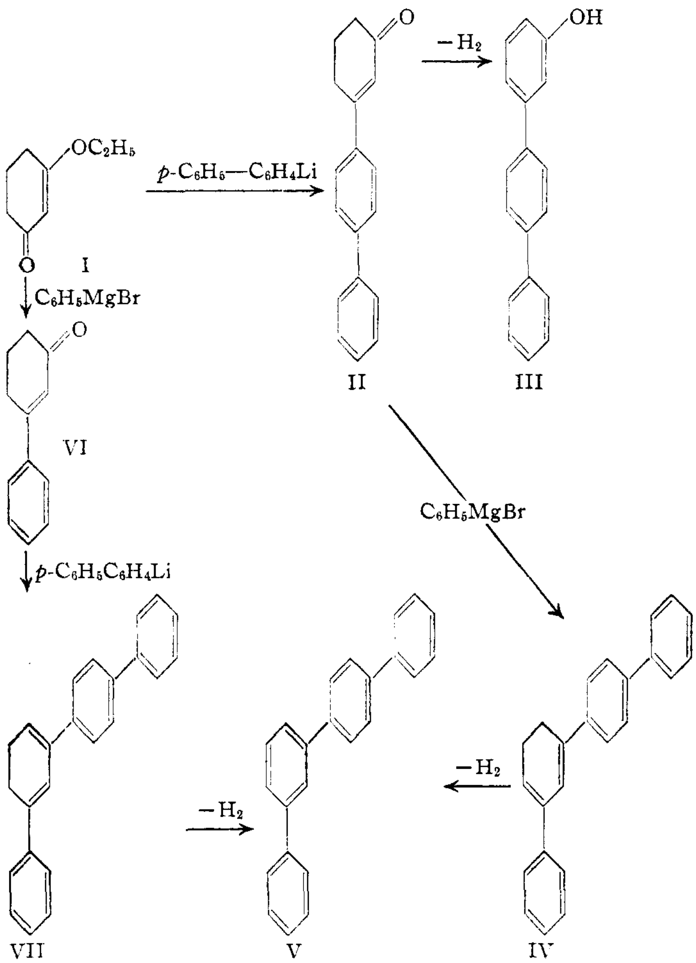
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND]

Synthesis of *m*-Diarylbenzenes

BY G. FORREST WOODS AND IRWIN W. TUCKER

We have shown[1] that *m*-diphenylbenzene can be obtained readily from the ethyl enol ether of dihydroresorcinol in three steps. In the course of this work it became apparent that a general method had become available for the synthesis of diarylbenzenes. This paper is the report of the extension of these reactions for the preparation of complex *m*-diarylbenzenes.

Dihydroresorcinol ethyl enol ether (I) reacted readily with *p*-biphenyllithium and from this reaction 3-(4-biphenyl)-Δ^2-cyclohexenone (II) was obtained. This ketone was dehydrogenated to *m*-(4-biphenyl)-phenol (III). Reaction of the biphenyl-Δ^2-cyclohexenone (II) with phenylmagnesium bromide afforded 1-phenyl-3-(4-biphenyl)-cyclohexadiene-1,3 (IV), and aromatization of this latter substance yielded *m*-phenyl-(4-biphenyl)-benzene (V). It is interesting to note that the reaction of dihydroresorcinol ethyl enol ether with the same organometallic reagents, but in the reverse order of use, led ultimately to the same aromatic compound (V) but did so *via* a different diene, 3-phenyl-1-(4-biphenyl)-cyclohexadiene-1,3 (VII), which is isomeric to (IV) in the position of the ethylenic links. These reactions are shown.



A complication arose in connection with the hydrocarbons IV, VII and V in that all three substances melted at essentially the same temperature and no reasonable lowering of the melting point in mixed melting point determinations could be observed. However, the difference between the aromatic substance (V) and the two dienes was established by carbon–hydrogen analyses and by hydrogenation experiments. It was found that the aromatic substance (V) would not undergo hydrogenation at room temperature and atmospheric pressure, while both of the dienes were readily reduced (approximately two moles of hydrogen were absorbed). But two products were always isolated from the reduction; one was 3-phenyl-1-(4-biphenyl)-cyclohexane, and the other was subsequently shown to be the aromatic hydrocarbon (V) instead of a geometrical isomer of the cyclohexane derivative, as we originally thought. The same results on reduction were obtained for either of the isomeric dienes, (IV) and (V). The various data on these hydrocarbons are collected in Table I.

There are two ways to account for the presence of the aromatic compound in the reduction of the dienes. The first is that the dienes undergo disproportionation during hydrogenation, or, and we believe more likely, that the dienes undergo some autoxidation on standing. Thus, in the earlier work[1] we found that 1,3-diphenylcyclohexadiene-1,3 became contaminated with some *m*-diphenylbenzene.

A structure of five rings, 1,3-di-(4-biphenyl)-cyclohexadiene-1,3 (VIII), was readily prepared by the reaction of 3-(4-biphenyl)-Δ^2-cyclohexenone (II) with *p*-biphenyllithium. This substance was also dehydrogenated to the aromatic compound *m*-di-(4-biphenyl)-benzene (IX). Here again, both the aromatic compound IX, and the diene VIII, melted at 262–264° and 265–269°, respectively, and gave no depression in a mixed melting point determination. The difference in these two substances had to be determined by analyses and the ability to undergo hydrogenation, the prod-

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[1] Woods and Tucker, THIS JOURNAL, **70**, 2174 (1948).

TABLE I

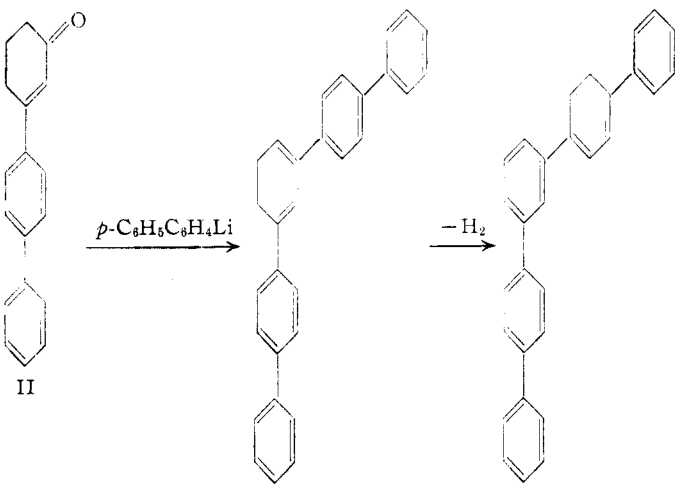
PHYSICAL AND ANALYTICAL VALUES FOR HYDROCARBONS

Hydrocarbon	M. p., °C.	Analyses, %			
		Calcd.		Found	
		C	H	C	H
1-Phenyl-3-(4-biphenyl)-cyclohexadiene-1,3 (VII)	162–163	93.46	6.54	93.47 93.57	6.51 6.52
3-Phenyl-1-(4-biphenyl)-cyclohexadiene-1,3 (IV)	161–162	93.46	6.54	93.50 93.58	6.70 6.61
m-Phenyl-(4-biphenyl)-benzene (V)	166–156	94.08	5.92	93.82 94.37	5.90 6.02
1-Phenyl-3-(4-biphenyl)-cyclohexane	89–90	92.26	7.74	92.62	7.35

uct of which was only one isomer of 1,3-di-(4-biphenyl)-cyclohexane.

Experimental

Preparation of 3-(4-Biphenyl)-Δ^2-cyclohexenone (II).—An ethereal solution (375 ml.) of *p*-biphenyllithium was prepared from 3.72 g. (0.535 mole) of lithium and 74 g. (0.32 mole) of 4-bromobiphenyl. To this was added 25 g. (0.18 mole) of dihydroresorcinol[1] ethyl enol ether dissolved in 100 ml. of ether, and the reaction mixture was heated under reflux for one-half hour. A small volume of ethyl alcohol was added to decompose the small amount of unreacted lithium. The lithium complex solution was decomposed with cold 5% sulfuric acid and subjected to steam distillation until all the biphenyl had been removed and the residue had solidified. This residue was extracted with benzene and the benzene solution washed with dilute sodium bicarbonate and finally with water. Removal of most of the benzene and addition of ethyl alcohol precipitated 40 g. (90% yield) of 3-(4-biphenyl)-Δ^2-cyclohexenone which melted at 166–167° after recrystallization from ethyl alcohol. *Anal.* Calcd. for $C_{18}H_{16}O$: C, 87.07; H, 6.49. Found: C, 86.59, 86.95; H, 6.63, 6.58.



The red 2,4-dinitrophenylhydrazone of this ketone, prepared in the usual manner, melted at 245–246° after thorough washing with ethyl alcohol. This derivative was too insoluble in the usual solvents to be recrystallized. *Anal.* Calcd. for $C_{24}H_{20}O_4N_4$: C, 67.28; H, 4.71. Found: C, 67.49, 67.56; H, 4.45, 4.98.

The semicarbazone of 3-(4-biphenyl)-Δ^2-cyclohexenone was prepared in the usual manner and melted at 238–245° with decomposition. *Anal.* Calcd. for $C_{19}H_{19}ON_3$: C, 74.70; H, 6.28. Found: C, 75.04; H, 5.93.

Preparation[2] of *m*-(4-Biphenyl)-phenol (III).—3-(4-Biphenyl)-Δ^2-cyclohexenone (3. g.), palladium-charcoal (1 g., 5%), and *p*-cymene (15 ml.) were heated vigorously under reflux for three hours. After cooling, 50 ml. of ethyl acetate was added, the mixture heated to boiling, and filtered. The filtrate was extracted three times with Claisen solution using 30 ml. for each extraction. The extract was then washed once with 25 ml. of benzene and once with 25 ml. of petroleum ether (60–80°). The alkaline extract was then diluted with 150 ml. of water, acidified with concentrated hydrochloric acid and boiled to remove most of the methanol. The solution was chilled and the solid phenol removed by suction filtration. *m*-(4-Biphenyl)-phenol, after decolorization and recrystallization from benzene, melted at 230–231°. *Anal.* Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.87; H, 5.83.

The phenylurethan of this phenol, prepared in the usual manner and recrystallized from benzene-petroleum ether, melted at 205–206.5°. *Anal.* Calcd. for $C_{25}H_{19}O_2N$: C, 82.17; H, 5.24. Found: C, 82.39; H, 5.00.

Preparation of 3-Phenyl-1-(4-biphenyl)-cyclohexadiene-1,3 (IV).—3-(4-Biphenyl)-Δ^2-cyclohexenone is rather insoluble in ether, so a slurry of the finely divided ketone (10 g., 0.04 mole) in 100 ml. of ether was added to 85 ml. of ether containing phenylmagnesium bromide prepared from 2 g. of magnesium and 18.7 g. of bromobenzene. The reaction mixture was refluxed for three hours at the end of which time the Grignard complex was decomposed with 100 ml. of 10% sulfuric acid. This solution was steam distilled to remove most of the impurities. The residue was extracted with benzene and the extract washed until neutral with water. Removal of most of the benzene and addition of 100 ml. of ethyl alcohol yielded 8.3 g. of product which, after recrystallization from toluene, yielded white crystalline 3-phenyl-1-(4-biphenyl)-cyclohexadiene-1,3.[3]

Preparation of 1-Phenyl-3-(4-biphenyl)-cyclohexadiene-1,3 (VII).—A solution of 8 g. of 3-phenyl-Δ^2-cyclohexenone[1] in 150 ml. of ether was added to 250 ml. of an ethereal solution containing *p*-biphenyllithium prepared from 0.98 g. of lithium and 18 g. of *p*-bromobiphenyl. The reaction mixture was allowed to stand several hours. Ethyl alcohol was added to decompose unreacted lithium and the metal addition complex was decomposed by addition of dilute sulfuric acid. The product[3] was isolated as in the previous procedure. A mixture of this substance and IV gave no observable melting point lowering.

Hydrogenation of the Dienes IV and VII.—Both 1-phenyl-3-(4-biphenyl)-cyclohexadiene-1,3 and 3-phenyl-1-(4-biphenyl)-cyclohexadiene-1,3 gave the same results on reduction. A typical example is given for the former. The diene (1.5 g.) in 25 ml. of ethyl alcohol was hydrogenated at atmospheric pressure using Raney nickel as catalyst at room temperature. The reduction arrested itself after absorption of 213 ml. of hydrogen. The time required for hydrogenation was approximately thirty minutes. Acetone was added to the mixture which was then filtered. Removal of acetone by heating on the steam bath and addition of a small amount of ethyl alcohol precipitated a small amount of solid, which, upon recrystallization from benzene, yielded *m*-phenyl-(4-biphenyl)-benzene melting at 166–167°. *Anal.* Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.29; H, 5.97. The filtrate, after removal of the above solid, when diluted with more ethyl alcohol deposited white crystalline ma-

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[2] Horning and Horning, THIS JOURNAL, **69**, 1359 (1947).

[3] For analytical and physical data see Table I.

terial (1.05 g.), which, upon recrystallization from benzene–ethyl alcohol, yielded 1-phenyl-3-(4-biphenyl)-cyclohexane.[3]

Preparation of *m*-Phenyl-(4-biphenyl)-benzene (V).—Dehydrogenation of each diene, IV and VII, gave the same results. 1-Phenyl-3-(4-biphenyl)-cyclohexadiene-1,3 (1.5 g.) dissolved in 7 ml. of *p*-cymene was refluxed briskly in the presence of 0.5 g. of palladium–charcoal (5%) for four hours. Benzene was added and the catalyst removed by filtration. Removal of most of the benzene and addition of ethyl alcohol precipitated 1.0 g. of solid which on recrystallization from benzene–alcohol yielded *m*-phenyl-(4-biphenyl)-benzene.[3]

Preparation of 1,3-Di-(4-biphenyl)-cyclohexadiene-1,3 (VIII).—A slurry of finely divided 3-(4-biphenyl)-Δ^2-cyclohexenone (II) (5.9 g.) in 100 ml. of ether was added to a solution of *p*-biphenyllithium in 125 ml. of ether prepared from 0.8 g. of lithium and 15.7 g. of *p*-bromobiphenyl. This mixture was refluxed for an hour at the end of which time a small amount of ethyl alcohol was added to destroy the remaining unreacted lithium. The lithium complex was hydrolyzed with dilute sulfuric acid and the solution subjected to steam distillation to remove some of the impurities. The solid residue, filtered, dried, powdered and crystallized from 500 ml. of toluene, weighed 11 g. and melted at 265–269°. *Anal.* Calcd. for $C_{30}H_{24}$: C, 93.70; H, 6.29. Found: C, 93.40, 93.75; H, 6.39, 6.34.

Hydrogenation of 1,3-Di-(4-biphenyl)-cyclohexadiene-1,3.—Finely divided 1,3-di-(4-biphenyl)-cyclohexadiene-1,3 (1.0 g.) in 50 ml. of toluene with Raney nickel absorbed 140 ml. of hydrogen (106% for two ethylenic links) at atmospheric pressure and room temperature in approximately forty minutes. At the end of the hydrogenation all the organic solid had dissolved. After filtration of the catalyst, addition of a small amount of ethyl alcohol precipitated a high melting solid (0.05 g.) which melted at 312° after recrystallization from toluene–ethyl alcohol and was not further studied. *Anal.* Found: C, 94.28, 94.41; H, 6.08, 6.02. Addition of more ethyl alcohol precipitated 0.75 g. of 1,3-di-(4-biphenyl)-cyclohexane which melted at 145–145.5° after recrystallization from toluene–ethyl alcohol. *Anal.* Calcd. for $C_{30}H_{28}$: C, 92.74; H, 7.26. Found: C, 92.86, 92.96; H, 7.33, 7.34.

Preparation of *m*-Di-(4-biphenyl)-benzene (IX).—1,3-Di-(4-biphenyl)-cyclohexadiene-1,3 (1.0 g.) dissolved in 10 ml. of phenetole to which had been added 0.3 g. of palladium-charcoal (5%) was refluxed for three hours. This mixture was then introduced into 300 ml. of boiling toluene, filtered while nearly at the boiling temperature and cooled. *m*-Di-(4-biphenyl)-benzene (0.8 g.) precipitated which upon recrystallization from toluene melted at 264–266°. *Anal.* Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.23, 94.42; H, 5.88, 5.96. This substance gave no depression with the precursor diene in a mixed melting point determination.

Summary

1. The utility of the ethyl enol ether of dihydroresorcinol for the preparation of some *m*-diarylbenzenes is shown.

2. The preparation of *m*-phenyl-(4-biphenyl)-benzene and *m*-di-(4-biphenyl)-benzene is reported.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Allylsodium with 2-Bromoöctane[1]

BY R. L. LETSINGER AND JAMES G. TRAYNHAM

In a previous publication[2] it was shown that benzylsodium couples readily with secondary bromides to give high yields of the Wurtz product. Since allylsodium is near benzylsodium in reactivity, one might expect it to behave similarly. In this paper we show that allylsodium does in fact react with 2-bromoöctane to give a 71% yield of 4-methyl-1-decene.

The allylsodium used in this work was prepared by the cleavage of diallyl ether with sodium metal.[3] That allylsodium was present in this cleavage mixture was shown by isolation of vinylacetic acid from the carbonated product. When fine sodium sand, high speed stirring, and a creased flask were employed, a 77% yield of vinylacetic acid was obtained.[4] The presence of the other expected product of the cleavage reaction, sodium alloxide, was demonstrated by the preparation of the 3,5-dinitrobenzoate derivative of allyl alcohol.

The reaction of the allylsodium–sodium alloxide mixture with 2-bromoöctane proceeded smoothly to give 4-methyl-1-decene. Hydrogenation of this olefin yielded 4-methyldecane.

We investigated the product of the Wurtz reaction carefully to determine whether it might be contaminated with allyl 1-methylheptyl ether. This ether could have been formed by a reaction of 2-bromoöctane with the sodium alloxide present. Both 4-methyl-1-decene and allyl 1-methylheptyl ether, since neither had been previously reported, were synthesized independently: the olefin from allyl bromide and 1-methylheptylmagnesium bromide, and the ether from allyl bromide and sodium 1-methylheptoxide. The physical constants of these compounds are given in Table I, and the infrared absorption spectra are given in Fig. 1. The spectra of the Wurtz product and 4-methyl-1-decene prepared by the Grignard reaction are identical, whereas allyl 1-methylheptyl ether shows strong absorption in a region of low absorption for the olefin. It is apparent from these data that the 4-methyl-1-decene prepared by this Wurtz reaction was entirely free of contamination by allyl

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[1] This investigation was supported by a grant from the Abbott Fund of Northwestern University.

[2] Letsinger, THIS JOURNAL, **70**, 406 (1948).

[3] The fact that diallyl ether can be cleaved by sodium to give allylsodium was previously observed by Morton, Magat and Letsinger, unpublished wok.

[4] Cleavage could also be accomplished under less favorable conditions, such as with sodium pellets, a low speed Hershberg stirrer, and a conventional flask; however, the yield of allylsodium was lower.