product was treated as described previously for hydrocarbon V.

A chloroform solution of the diene was aromatized with 1 g. of bromine. The organic product isolated was recrystallized from petroleum ether (b.p. 100–120°) affording white crystalline material, m.p. 187.5–188.5°. The melt produced crystals which, upon further heating, melted at 206–207°; yield: 1.2 g. (52%). The mixed melting point with the product obtained by Method A was at 205–207°. Recrystallization of this sample from petroleum ether (b.p. 100–120°) gave crystalline material, m.p. 186–188°.

Preparation of III, III-*diphenyl-[2,5]quinque[4,3,4]phenyl* (VII). 2,5-Diphenyl-3-(4-xenyl)-2-cyclohexenone in dry benzene was added to a 4-xenyllithium solution prepared from bromobenzene and *n*-butyllithium. The reaction complex was decomposed with cold dilute sulfuric acid and the resulting organic product was submitted to steam distillation from dilute sulfuric acid. Isolation of the crude diene was accomplished as described for the preparation of hydrocarbon V.

The diene, in chloroform, was aromatized with 0.8 g. of bromine. The aromatic product was isolated as described previously. The product was recrystallized several times from petroleum ether (b.p. 100–120°) toluene, petroleum ether (b.p. 100–120°), and ethyl acetate, respectively. A white crystalline material, m.p. 230–233°, was obtained; yield, 0.96 g. (36%). ϵ_{max} 7.56 × 10^4 (λ_{max} 268 mμ).

Anal. Calcd. for $C_{42}H_{30}$: C, 94.34; H, 5.66. Found: C, 94.24; H, 5.81.

Preparation of II-*phenyl-[3]*-III-*phenyl-[2]-quater[4,4]-phenyl* (XII). An ethereal solution of 4′-bromo-*m*-terphenyl[5] (10.0 g.) was treated with 19 ml. of 0.86*N* *n*-butyllithium at room temperature. The mixture was cooled to −70° and stirred at this temperature for 1 hr. Cobalt(II) chloride (2.08 g.) was added as a slurry in ether. The mixture was stirred at −70° for several hours and then allowed to warm slowly to room temperature. The reaction mixture was poured onto an ice water–sulfuric acid mixture. The organic product was extracted with ether, washed with sodium bicarbonate and then with water, and finally dried over magnesium sulfate. Upon concentration of the ethereal solution, a viscous material was obtained. This material was chromatographed on alumina with petroleum ether (b.p. 60–80°) as the eluent. Fractions of 30 ml. volume each were collected. The first two fractions contained 6 g. of unchanged 4′-bromo-*m*-terphenyl. Fraction three afforded 1 g. of *m*-terphenyl. Fractions four through six afforded 1.2 g. of a white solid which was recrystallized from petroleum ether (b.p. 60–80°), m.p. 223–225°; ϵ_{max} 3.3 × 10^4 (λ_{max} 286.5 mμ) and ϵ_{max} 6.5 × 10^4 (λ_{max} 249 mμ). Molecular weight: Calcd., 458.6. Found (cryoscopic), 472.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.19; H, 5.99.

An attempt to use atmospheric oxygen to affect the coupling of the 4′-*m*-terphenyllithium yielded considerable phenolic material with no isolable sexiphenyl.

Preparation of II-*phenyl-[3]*-IV-*phenyl[2]quinque[4,3,4]-phenyl* (XIII). *n*-Butyllithium (18 ml. of 0.78*N* solution) was added, with stirring, to 4.3 g. of 4′-bromo-*m*-terphenyl. 1-(3-Keto-2-cyclohexenyl)-2,4-diphenylbenzene (XI)[2] (3.9 g.) was added as a slurry in ether. The addition complex was decomposed in an ice–sulfuric acid mixture. The ethereal layer was washed with sodium bicarbonate and then with water. The ether was concentrated to half its volume. The solid which precipitated upon concentration was filtered and recrystallized from isopropyl alcohol-benzene mixture; yield 4.0 g. of the diene (62%); m.p. 186–188°.

A solution of 1 g. of the diene in 50 ml. of *p*-cymene was refluxed with 0.3 g. of palladium on carbon for 1 hr. This mixture while hot was filtered through a short column of alumina (2 in. long, 1 in. diameter). The resulting clear solution was concentrated, affording white crystalline material. This solid was recrystallized from isopropyl alcohol-benzene; yield: 0.9 g. (82.5% for aromatization), m.p. 266–267°.

Molecular weight: Calcd. 534.7. Found (cryoscopic), 543. ϵ_{max} 6.7 × 10^4 (λ_{max} 247.9 mμ) and ϵ_{max} 4.8 × 10^4 (λ_{max} 276 mμ).

Anal. Calcd. for $C_{42}H_{30}$: C, 94.34; H, 5.66. Found: C, 94.37; H, 5.90.

Acknowledgment. This research was supported in part by the United States Air Force under Contract No. 33(616)–5063, monitored by the Aeronautical Research Laboratory, Wright Air Development Center.

College Park, Md.

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

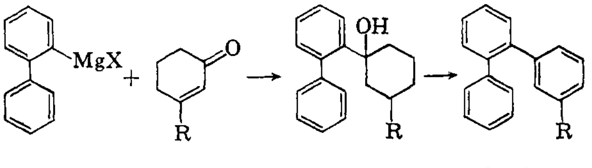
Synthesis of Polyphenyls Containing *ortho* Linkages

G. FORREST WOODS and FRANK SCOTTI

Received May 13, 1960

Two methods are reported for the synthesis of polyphenyls containing *ortho* linkages. Also included are the preparations of some 2-arylcyclohexanones, 1,2-diarylcyclohexanols, 2-aryl-2-cyclohexenones, and some new polyphenyls.

A general method for the introduction of an *ortho* link into a polyphenyl has been dependant on the conversion of a 2-halosubstituted biphenyl to a Grignard reagent and the reaction[1] of the latter with a 3-substituted 2-cyclohexenone as shown below:



This process results in an *ortho* link in the terminal position of the polyphenyl molecule. A method was desired which would make possible the introduction of an *ortho* link not only in the terminal position but in any position within the structure. Synthetic procedures for this have now been developed.

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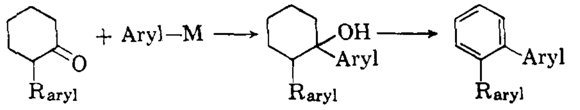
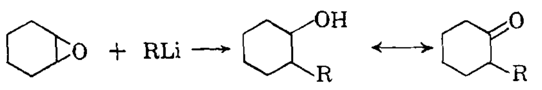
[1] G. F. Woods, A. L. Van Artsdale, and F. T. Reed, *J. Am. Chem. Soc.*, 72, 3221 (1950).

The first procedure employs the reaction of 2-arylcyclohexanone with an appropriate arylmetallic reagent:



I II III

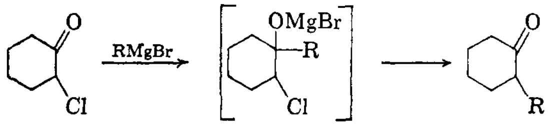
Two approaches were utilized for the preparation of the 2-arylcyclohexanone. The first employed the reaction of cyclohexene oxide with 4-xenyl- and 3-xenyllithium[2] followed by oxidation of the resultant alcohol.



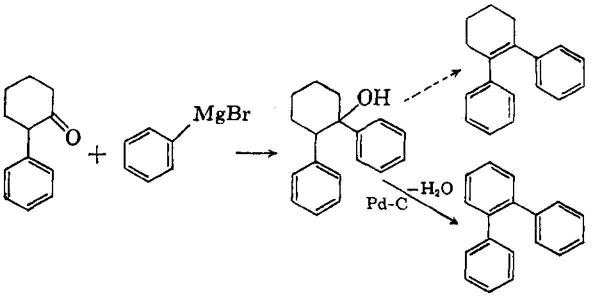
IV I

In addition to these two alcohols, commercial 2-phenylcyclohexanol was also oxidized to 2-phenylcyclohexanone. Oxidation of the three alcohols was effected with chromic anhydride in 80% acetic acid according to Cook's[3] procedure. The product was generally contaminated with starting alcohol. An Oppenauer oxidation of 2-(4-xenyl)-cyclohexanol employing benzoquinone provided 2-(4-xenyl)cyclohexanone in 80% yield on the basis of the weight of semicarbazone derivative. However, oxidation by the Oppenauer procedure proved to be too cumbersome to be of large scale preparative value. Actually, oxidation of 2-arylcyclohexanols was utilized primarily as an alternate method to establish partially the structure of certain of the 2-substituted cyclohexanones.

The second approach for the preparation of 2-arylsubstituted cyclohexanones employed the reaction of 2-chlorocyclohexanone with the Grignard reagents[4]: C_6H_5-, *p*- and *m*-xenyl, and *p*-BrC_6H_4-MgBr.



The proposed scheme of synthesis was tested by the preparation of *o*-terphenyl:

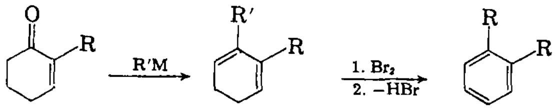


It is surprising that the Grignard addition product, 1,2-diphenylcyclohexanol, is so stable that it survived attempted dehydration by steam distillation from a 10% sulfuric acid medium and also distillation at atmospheric pressure.[5] However, simultaneous dehydration and dehydrogenation occurred with palladium on charcoal at 300° and *o*-terphenyl was obtained in good yield.[6]

Table I gives the alcohols prepared and aromatized with palladium on charcoal.

The above method for the synthesis of *ortho*-linked polyphenyls cannot be used if a halopolyphenyl is desired, for aromatization with palladium on charcoal (or other dehydrogenation catalysts) results in dehydrohalogenation.

To avoid the use of catalysts the following reaction scheme was adopted: Bachmann[7] prepared 2-phenyl-2-cyclohexenone by bromination of 2-phenylcyclohexanone followed by dehydrobromination of the product with 2,6-lutidine.



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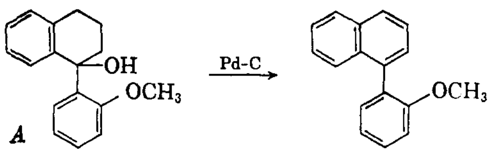
(2) B. G. McKusick, *J. Am. Chem. Soc.*, **70**, 1977 (1948).

(3) J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 71, (1936).

(4) M. S. Newman and M. D. Farbman, *J. Am. Chem. Soc.*, **66**, 1550 (1944). M. S. Newman and W. T. Booth, *J. Org. Chem.*, **12**, 737 (1947).

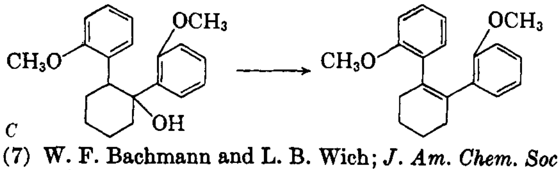
(5) The corresponding alcohol di-substituted in the 4,4′ position with —OCH_3 underwent dehydration during decomposition of the Grignard addition complex with ammonium chloride. G. P. Mueller and R. May, *J. Am. Chem. Soc.*, **71**, 3313 (1949).

(6) A literature survey disclosed some interesting aspects of the reaction of cyclohexanols under such conditions. For instance, while the dehydration and dehydrogenation of *A* occurs [M. Orchin, *J. Am. Chem. Soc.*, **70**, 495 (1948).], J. Plesek and M. Mink [*Collection Czech. Chem. Commun.* **22**, 1688 (1957)] report that *B* gives *o*-terphenyl with palladium on carbonate-activated alumina but that palladium on acid treated alumina was not catalytically effective. R. L. Huang [*J. Chem. Soc.*, 3655 (1954)] found that *C* did not aromatize with palladium on charcoal at 300° but the dehydration product was isolated.



A

B

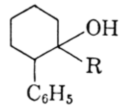
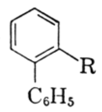
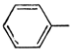
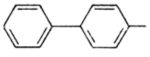
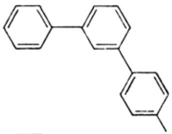
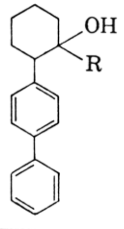
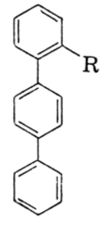
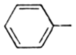
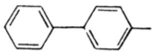
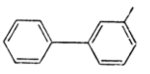


C

(7) W. F. Bachmann and L. B. Wich; *J. Am. Chem. Soc.*, **72**, 3388 (1950).

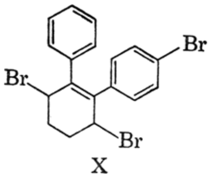
TABLE I

CYCLOHEXANOLS PREPARED, DEHYDRATED AND DEHYDROGENATED

		Compound	R
		V	
		VI	
		VII	
		VI	
		VIII	
		IX	

This procedure was earlier employed in this work except that the crude bromination mixture was submitted directly to dehydrobromination. Subsequently, chlorination of the ketone with sulfuryl chloride followed by dehydrochlorination in like manner was used.

To establish the validity of these reactions the first synthesis attempted from the unsaturated ketone was that of *o,p*-quaterphenyl, a known compound having a relatively high melting point and fairly distinctive ultraviolet absorption spectrum. This was attempted by the addition of 4-xenylmagnesium bromide to 2-phenyl-2-cyclohexenone. The reaction was complex, for a 47% yield of product from 1,4-addition and only an 8% yield of 1,2-addition product was obtained. However, reaction of 4-xenyllithium was predominately by 1,2-addition[8] and the product was aromatized by bromine addition or with palladium-charcoal (in this case) to the desired *o,p*-quaterphenyl (VI) which had been prepared also by the first method. In like manner, 4-bromophenyllithium was added to 2-phenyl-2-cyclohexenone and the diene resulting from hydrolysis and dehydration was aromatized with bromine addition–hydrogen bromide elimination to yield 4-bromo-*o*-terphenyl. This aromatization, however, was unlike the other similar aromatizations since a crystalline compound, presumably the tribromide X, can be isolated. This substance is unstable and attempted recrystallization always caused dehydrobromination. Likewise, the infrared spectrum taken of the material as a melt was that of 4-bromo-*o*-terphenyl while its ultraviolet spectrum is very much like that of *cis*-stilbene.



X

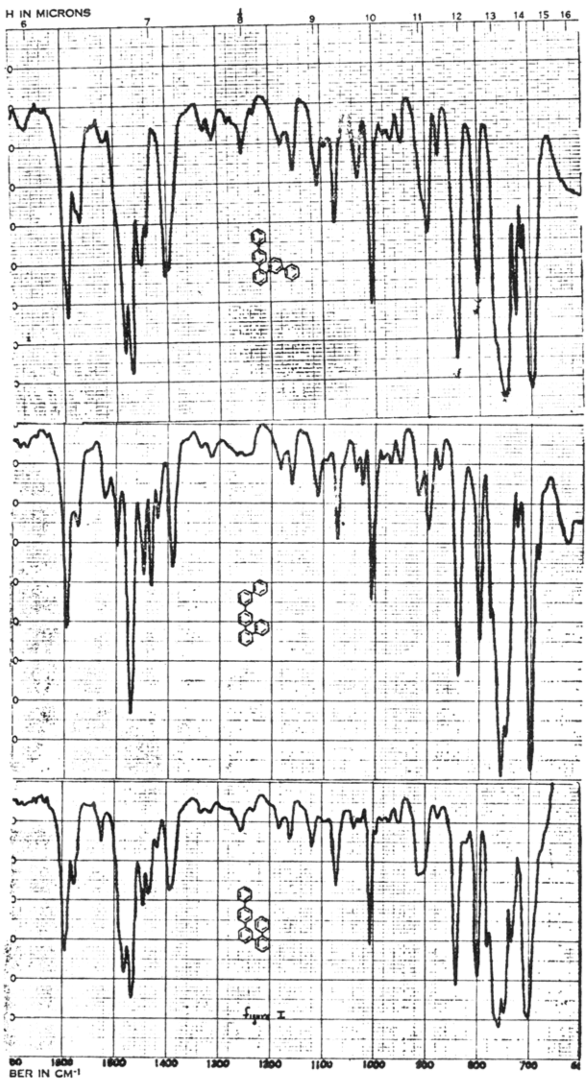


Fig. 1. Infrared spectra of three quinquephenyls

In order to demonstrate the utility of 4-bromo-*o*-terphenyl it was converted to the lithium derivative which was allowed to react with 3-phenyl-2-cyclohexenone. The product of this reaction was dehydrated to the diene and the latter aromatized to quinque[2.4.3]phenyl melting at 119.5–120°—some 20° higher than VII (the same compound prepared by an alternate synthesis). The lower melting material recrystallized from petroleum ether and seeded with the higher melting material provided higher melting product.

There are three particular isomers of the eighteen possible linear quinquephenyls, each of which contain an *ortho*, a *meta*, and a *para* link, but in a different order:

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[8] A. Luttringhaus, *Ber.*, 67, 1602 (1934).

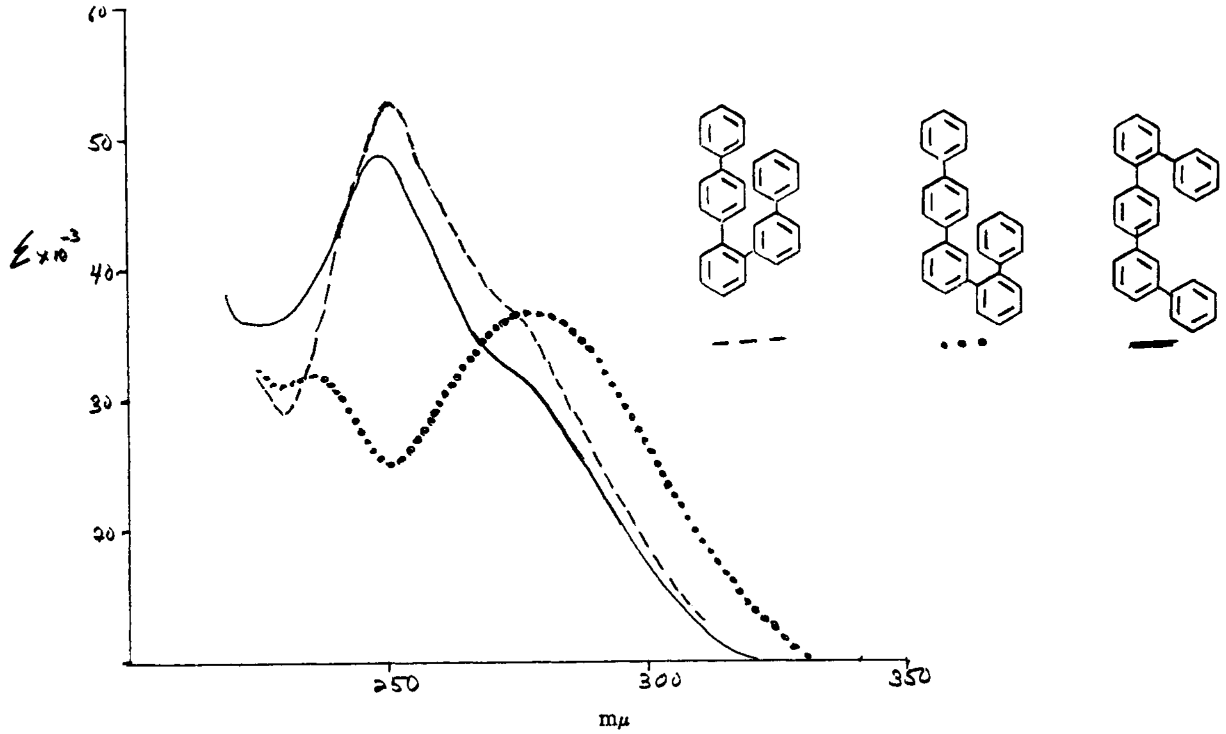
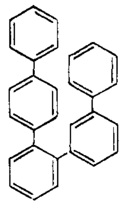
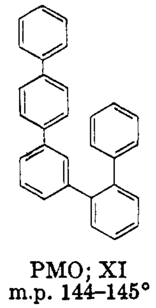


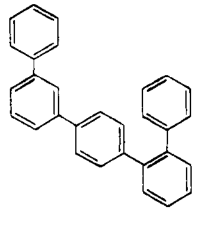
Fig. 2. Ultraviolet spectra of three quinquephenyls



POM; IX
m.p. 105–106°



PMO; XI
m.p. 144–145°



MPO; VII
m.p. 119–120°

Substances IX and VII were prepared in this work and the earlier reported synthesis of XI was repeated. The infrared spectra, Fig. 1, of the three quinquephenyls show slight differences, probably more than might have been expected.[9] The ultraviolet spectra, Fig. 2, showed that XI is considerably different from VII and IX. Vapor phase chromatography did not distinguish between VII and XI but partially resolved the two mixtures: (1) IX and XI and (2) VII and IX.

EXPERIMENTAL[10]

Preparation of 2-(3-xenyl)cyclohexanol and 2-(4-xenyl)-cyclohexanol (IV). The appropriate bromobiphenyl (0.11 mole) dissolved in 50 ml. of anhydrous ether was added dropwise to a mixture of 0.22 mole of lithium in 25 ml. of ether. After the formation of the aryllithium, 9.8 g. (0.10 mole) of cyclohexene oxide in 10 ml. of ether was added and the resulting solution was stirred for 1 hr. The mixture was decomposed with water.

2-(3-Xenyl)cyclohexanol was isolated as a heavy oil which distilled at 160°/0.08 mm.; 8.5 g. (33.7%). After standing for a considerable period, the material crystallized and was recrystallized from petroleum ether (b.p. 80–100°); m.p. 60.5–62°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.43; H, 7.98.

The ethereal solution containing 2-(4-xenyl)cyclohexanol had a white precipitate which proved to be *p*-quaterphenyl and it was removed by filtration. Evaporation of the filtrate yielded crystalline material which, upon two recrystallizations from petroleum ether (b.p. 80–100°), provided 2-(4-xenyl)cyclohexanol, m.p. 131–133°; yield: 11.5 g. (46%).

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.47; H, 8.20.

Oxidation of phenyl and xenylcyclohexanols to the corresponding ketones (I). To a glacial acetic acid solution of the phenylcyclohexanol was added an equimolar solution of chromic anhydride in 80% acetic acid.[3] The mixture was maintained at room temperature for 8–12 hr. after which the acetic acid was removed under reduced pressure and the residue was dissolved in ether. The ethereal solution was washed with water, then with a sodium carbonate solution (from which an approximately 25% yield of ω-benzoylvaleric acid was isolated). The ethereal solution was dried and distilled. 2-Phenylcyclohexanone was obtained (15 g., 37%), b.p. 160/16 mm.; m.p. 53–55° after recrystallization from petroleum ether (b.p. 60–80°). This material had a fairly strong absorption band at 3400 cm.$^{-1}$ characteristic of an —OH stretching frequency.

Oxidation of the xenylcyclohexanols was accomplished in the same manner. The isolation of 2-(3-xenyl)cyclohexanone from the acetic acid oxidation medium was effected by pouring the acetic acid solution into an equal volume of water. The aqueous solution was extracted three times with benzene. The combined benzene extracts were washed with aqueous potassium hydroxide and with water. Removal of the solvent under reduced pressure left an oil which could not be induced to crystallize. The material was

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[9] Private communication, Prof. Ellis R. Lippincott.

[10] All ultraviolet spectra were obtained in isooctane with a Beckman model DK Recording Spectrophotometer. Melting points are corrected.

taken up in 95% ethanol and the *2,4-dinitrophenylhydrazone* of the ketone was prepared in the usual manner; yield: 34.4%; m.p. 145–146°.

Anal. Calcd. for $C_{24}H_{23}O_4N_4$: C, 66.81; H, 5.37. Found: C, 66.76; H, 5.12.

In the instance of the preparation of 2-(4-xenyl)cyclohexanone, the excess acetic acid was removed under reduced pressure, and the residue was diluted with water and extracted with ether. The combined ether extract was washed with sodium carbonate and with water and was dried. Evaporation of the solvent provided crystalline material which was recrystallized from petroleum ether (b.p. 60–80°); m.p. 95–100°. This material also showed an —OH stretching frequency at 3400 cm.$^{-1}$ From 0.2 g. of this material 0.15 g. of *semicarbazone,* m.p. 207–208°, was obtained.

Anal. Calcd. for $C_{19}H_{21}ON_3$: C, 74.24; H, 6.89. Found: C, 74.31; H, 6.90.

The *ketone* was isolated in the usual manner from the acid hydrolysis of the semicarbazone in ethanol, m.p. 103–105°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.15; H, 7.03.

An alternate preparation of the above ketone was accomplished as follows. A solution, in 120 ml. of dry benzene, of 2.0 g. of 2-(4-xenyl)cyclohexanol, 12 g. of benzoquinone, and 3.0 g. of aluminum isopropoxide was stirred for 8 days at room temperature. Water was added and the whole was submitted to steam distillation. The steam pot residue was acidified with dilute sulfuric acid and extracted with ether. The ethereal extract was swirled, not shaken, with 5% aqueous potassium hydroxide and this treatment continued until the ethereal solution turned red. The ethereal solution was then further shaken with alkali until no more color was removed. The organic layer was washed with water, dried, and then concentrated. The resultant oil was dissolved in methanol and the semicarbazone was prepared in the usual manner; yield: 1.85 g. (76.5%); m.p. 207–208°. No depression of melting point was observed with admixture of the above sample.

Preparation of 2-substituted cyclohexanones from 2-chlorocyclohexanone. 2-Phenylcyclohexanone was prepared in 45% yield[4] employing the addition of phenylmagnesium bromide to 2-chlorocyclohexanone followed by rearrangement of the addition product.

2-(4-Xenyl)cyclohexanone was prepared similarly. 4-Xenylmagnesium bromide was prepared by the addition of 46.6 g. of 4-xenyl bromide dissolved in tetrahydrofuran to 5.0 g. of magnesium turnings in a minimum of tetrahydrofuran. To the Grignard solution 26.4 g. of 2-chlorocyclohexanone, dissolved in 60 ml. of ether, was added. Most of the ether and tetrahydrofuran was removed by distillation and 200 ml. of dry benzene was added. The benzene mixture was refluxed for 8 hr. and subsequently hydrolyzed with aqueous ammonium chloride. The benzene layer was withdrawn and the aqueous layer was extracted twice with ether. The combined extracts were dried, filtered, and concentrated. The crude oil was distilled under high vacuum employing a crude distillation apparatus consisting of a round bottom flask, elbow adapter, and receiver (oil bath: 220°; 0.05 mm.). The distillate crystallized and was recrystalled twice from ether, yielding 25.0 g. (50%) of 2-(4-xenyl)cyclohexanone, m.p. 106–107°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.18; H, 7.35.

The semicarbazone was formed in the usual manner, m.p. 207–208°; no depression on admixture with the sample prepared by the earlier procedure.

2-(3-Xenyl)cyclohexanone was prepared by the reaction of 3-xenylmagnesium bromide prepared in ether but otherwise handled as in the preparation of the above 2-(4-xenyl)-cyclohexanone. The distillate was an oil which could not be induced to crystallize; yield: 40%. The 2,4-dinitrophenylhydrazone was prepared in the usual manner, m.p. 145–146°. It was identical with the sample prepared earlier by oxidation of the alcohol.

2-(4-Bromophenyl)cyclohexanone was prepared from 4-bromophenylmagnesium bromide in ether to which 2-chlorocyclohexanone was added. The product was isolated as described above. The bromo ketone solidified on standing and was recrystallized from petroleum ether (b.p. 80–100°); m.p. 82.5–83°); yield: 18%.

Anal. Calcd. for $C_{12}H_{13}OBr$: C, 56.93; H, 5.18. Found: C, 57.08; H, 5.16.

The *2,4-dinitrophenylhydrazone* was prepared in the usual manner; m.p. 143–144°.

Anal. Calcd. for $C_{18}H_{17}N_4O_4Br$: C, 49.90; H, 3.96. Found: C, 50.02; H, 4.08.

Preparation of o-terphenyl (V). To a slight excess of phenylmagnesium bromide was added 10.0 g. of 2-phenylcyclohexanone. The Grignard addition complex was decomposed with ammonium chloride solution and the ether layer was separated, washed with water, and dried. After removal of the solvent, the residue was distilled, a fore-run of biphenyl was rejected. 1,2-Diphenylcyclohexanol (b.p. 160°/10 mm.) crystallized and was recrystallized from petroleum ether (b.p. 30–60°); yield: 51%, m.p. 64–65°.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.73; H, 7.99.

1,2-Diphenylcyclohexanol (6.0 g.) was dehydrated and dehydrogenated with a small amount of 10% palladium on charcoal. The material, in a small flask equipped with a condenser fitted so gas evolution could be detected, was heated at 290°. Rapid evolution of gas was observed as was considerable bumping (caused by water condensate). After the evolution of gas had ceased the organic material was dissolved in petroleum ether (b.p. 30–60°) and the whole solution was passed through a short chromatographic column of alumina. After a small wash, the petroleum ether was removed on a steam bath and the resulting oil was dissolved in methanol. After chilling, crystalline material precipitated which yielded 4.25 g. (78%) of terphenyl; m.p. 58–59°, no depression with an authentic sample.

o,p-Quaterphenyl (VI). Method A. 2-(4-Xenyl)cyclohexanone (5.0 g.) in 30 ml. of ether was added to an excess of phenylmagnesium bromide. The addition complex was decomposed with ammonium chloride solution. The ether layer was separated and submitted to steam distillation from a 5% aqueous potassium carbonate solution. After most of the biphenyl had steam distilled, the residual viscous oil was dissolved in ether. The ethereal solution was dried and the ether was evaporated on a steam bath. The resulting oil was dissolved in petroleum ether (b.p. 60–80°) and upon chilling crystallization occurred. Two recrystallizations from petroleum ether (b.p. 60–80°) yielded 6.0 g. (92%) of 1-phenyl-2-(4-xenyl)cyclohexanol; m.p. 84–85°.

Anal.. Calcd. for $C_{24}H_{24}O$: C, 87.76; H, 7.36. Found: C, 88.05; H, 7.43.

The above alcohol (3.0 g.) was treated with palladium on charcoal as in the preparation of *o*-terphenyl except that petroleum ether (b.p. 60–80°) was used. During the process of concentration of the solvent after chromatography material crystallized. Recrystallization from petroleum ether (b.p. 60–80°) yielded 2.0 g. (71%) of *o,p*-quaterphenyl; m.p. 119–119.5°. Mol. wt. (cryoscopic): 294. (Calcd.: 306), λ_{max} (ϵ 3.0 × 10^4 248 mμ), (ϵ 2.6 × 10^4 275 mμ).

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.15; H, 5.83.

Method B. In like manner 2-phenylcyclohexanone was added to an excess of Grignard reagent prepared from 4-xenylmagnesium bromide in tetrahydrofuran. The Grignard complex was decomposed as above and the cold ether layer was filtered to remove *p*-quaterphenyl. Steam distillation, as above, was accomplished. Upon cooling the residue in the steam pot the oily material crystallized and was isolated by suction filtration and recrystallized from methanol. The yield of 2-phenyl-1-(4-xenyl)cyclohexanol was 8.1 g.

(86%); m.p. 135–137°. This is an isomer of the preceding alcohol.

Anal. Calcd. for $C_{24}H_{24}O$: C, 87.76; H, 7.36. Found: C, 87.92; H, 7.08.

Treatment of 6.0 g. of this alcohol with palladium on charcoal as described above yielded 4.5 g. of *o,p*-quaterphenyl; m.p. 119–119.5°, identical with the earlier prepared sample.

Preparation of quinque[4.2.4]phenyl (VIII). An ethereal solution of 2-(4-xenyl)cyclohexanone was added to the Grignard reagent prepared from 4-xenyl bromide. The product was worked up as described above; crystalline material settled out in the steam pot residue. It was recrystallized from benzene–petroleum ether (b.p. 80–100°). 1,2-Di(4-xenyl)cyclohexanol 5.8 g. (72%); m.p. 146–147.5° was obtained.

Anal. Calcd. for $C_{30}H_{28}O$: C, 89.07; H, 6.98. Found: C, 88.96; H, 6.76.

The aromatization of the alcohol was accomplished as earlier described. The material was recrystallized from benzene–petroleum ether (b.p. 80–100°); yield: 94%; m.p. 182–4°: $\lambda_{\max} = 267$ mμ (ϵ 5.6 × 10^4).

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.23; H, 5.74.

Preparation of quinque[3.2.4]phenyl, (IX). This compound was prepared from the reaction of 3-xenylmagnesium bromide with 2-(4-xenyl)cyclohexanone in the manner described above. After steam distillation the oily residue was dissolved in ether and the ethereal solution was dried and concentrated. The residual oil recrystallized from methanol; yield: 6.4 g. (80%); m.p. 111–115°. To obtain pure material the crude alcohol was dissolved in petroleum ether (b.p. 80–100°) and chromatographed on an alumina column. The column was developed with a mixture of 87% petroleum ether (b.p. 80–100°) and 13% benzene. *m*-Quaterphenyl was isolated after a small amount of eluate had been collected. The column was then eluted with benzene–petroleum ether (b.p. 80–100°) 1:1. Concentration of the eluate provided solid material which was recrystallized from methanol, to yield 1-(3-xenyl)cyclohexanol; m.p. 116–119°.

Anal. Calcd. for $C_{30}H_{28}O$: C, 89.07; H, 6.98. Found: C, 89.10; H, 6.66.

Elution of the column with methanol provided a small amount of the starting ketone as determined by its 2,4-dinitrophenylhydrazone. From 2.5 g. of the crude alcohol, 2.0 g. of the desired alcohol was isolated.

The above alcohol was aromatized with palladium charcoal as described earlier and the product was dissolved in petroleum ether (b.p. 80–100°) and passed through a short alumina column. After evaporation of the solvent, the residue was recrystallized from methanol to yield quinque[3.2.4]phenyl; m.p. 105–106°; yield: 68%. Mol. wt. (cryoscopic): 376. (Calcd.: 382). $\lambda_{\max}$ 250 mμ (ϵ 5.3 × 10^4).

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.26; H, 5.70.

Three grams of crude alcohol provided the desired hydrocarbon in 63% yield after two recrystallizations from methanol.

Quinque[2.4.3]phenyl, (VII). A solution of 2-phenylcyclohexanone in ether was added to the lithium derivative of 4-bromo-*m*-terphenyl[11] (interchange with *n*-butyllithium) also in ether. The reaction mixture was stirred for an hour, then hydrolyzed with water. The ether layer was separated, dried with magnesium sulfate, and concentrated. The resulting oil was dissolved in petroleum ether (b.p. 80–100°), and the solution was passed through an alumina column. After the hydrocarbons and the aryl halide had been eluted, the column was eluted with methanol. Concentration of the methanol provided crystalline material which was recrystallized twice from methanol; yield: 44% of 2-phenyl-1-(4-*m*-terphenylyl)cyclohexanol; m.p. 116–118°.

Anal. Calcd. for $C_{30}H_{28}O$: C, 89.07; H, 6.98. Found: C, 88.99; H, 6.92.

This alcohol was aromatized with palladium charcoal at 300–310° in the manner previously described. The resulting mixture was dissolved in petroleum ether (b.p. 60–80°), and passed through a short alumina column. Evaporation of the solvent provided an oil which was redissolved in petroleum ether (b.p. 60–80°). Chilling of the solution provided crystalline material, which was recrystallized from petroleum ether (b.p. 60–80°); yield of quinque[2.4.3]phenyl 74%; m.p. 99–99.5°, $\lambda_{\max}$ 248 mμ (ϵ 4.9 × 10^4).

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.41; H. 5.78. Mol. wt. (cryoscopic) 400. Calcd. 382.

If the above material is dissolved in petroleum ether (b.p. 60–80°) and the solution seeded with the material obtained by the alternate synthesis (see below), product of m.p., 119.5–120° is obtained (no depression of melting point of the mixture of substances).

2-Phenyl-2-cyclohexenone. A solution of 4.3 g. of sulfuryl chloride was added to a chilled solution of 5 g. of 2-phenyl-2-cyclohexanone in 5 ml. of carbon tetrachloride. After the addition was complete, the mixture was allowed to warm to room temperature and was stirred for 2 hrs. The solution was then washed once with water, three times with aqueous sodium bicarbonate, and finally with water. The solution was dried with magnesium sulfate, and was concentrated under reduced pressure. The resulting oil crystallized from methanol. 2-Chloro-2-phenylcyclohexanone was recrystallized from methanol; yield 1.4 g. (23%); m.p. 122–123°.

Anal. Calcd. for $C_{12}H_{13}OCl$: C, 69.06; H, 6.28. Found: C, 69.00; H, 6.11.

The product was dehydrohalogenated with 2,6-lutidine following Bachmann's[7] directions to yield 2-phenyl-2-cyclohexenone; m.p. 95–96° (2,4-dinitrophenylhydrazone, m.p. 163–165°), yield: 90%. If the crude oil from chlorination was treated with 2,6-lutidine directly, an 85% yield from 2-phenylcyclohexanone was obtained.

Reaction of 2-phenyl-2-cyclohexenone with 4-xenylmagnesium bromide. 2-Phenylcyclohexenone (3 g.) in 30 ml. of ether was added to the Grignard reagent prepared from 4-xenyl bromide in tetrahydrofuran. The Grignard complex was decomposed with dilute sulfuric acid. The ethereal layer was submitted to steam distillation; the steam pot residue was extracted with ether and the ether layer was dried with magnesium sulfate after having been washed with water. The ether was evaporated and the resulting oil was dissolved in *p*-cymene. After addition of palladium charcoal, the solution was heated under reflux for several hours. After filtration, the *p*-cymene was distilled off, and the residual oil was dissolved in petroleum ether (b.p. 60–80°). This solution was submitted to chromatographic adsorption on alumina, and fractions of 100 ml. were collected. The third and fourth fractions contained *o,p*-quaterphenyl (VI) m.p. 119–119.5°, yield 0.4 g. (7.7%); no depression on admixture with earlier sample. The alumina column was eluted with methanol. Evaporation of the methanol left an oil which was then dissolved in ethanol; it was allowed to react with an excess of 2,4-dinitrophenylhydrazine in the usual manner, and 4.2 g. yield of the yellow 2,4-dinitrophenylhydrazone of 3-(4-xenyl)-2-phenylcyclohexanone was obtained (48% based on 1,4-addition of the Grignard reagent); m.p. 227–228° after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{30}H_{26}N_4O_4$: C, 71.13; H, 5.17. Found: C, 70.89; H, 5.11.

o,p-Quaterphenyl, (VI). 2-Phenyl-2-cyclohexenone was added to 4-xenyllithium in ether (*n*-butyllithium interchange). The reaction medium was poured into ice water–sulfuric acid. The ether layer was separated and submitted to steam distillation; the oil in the steam pot solidified. This was isolated and recrystallized from isopropyl alcohol; yield, 3.9 g. (73%); m.p. 125–127°. A good analysis could not be obtained in the diene; it was therefore aromatized with palladium charcoal in *p*-cymene. The reaction mixture was

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[11] G. F. Woods, D. D. Centola, H. E. Ruskie, and C. D. Mller, *J. Am. Chem. Soc.*, **82**, 522 7 (1960).

filtered, and the excess *p*-cymene was removed by distillation. Recrystallization of the residue from petroleum ether (60–80°) yield *o,p*-quaterphenyl (VI), (1.05 g.); m.p. 119–119.5°.

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.34; H, 6.10.

4-Bromo-o-terphenyl. A solution of 2-phenyl-2-cyclohexenone (3 g.) in ether was added dropwise with stirring to a solution of *p*-bromophenyllithium prepared from the reaction of *p*-dibromobenzene with *n*-butyllithium. The reaction mixture was decomposed with dilute sulfuric acid. The ether layer was separated and submitted to steam distillation. An oily residue remained in the steam pot. The oil was extracted with ether and the ethereal solution was dried with magnesium sulfate. The ether was removed and the resulting oil was dissolved in 20 ml. of chloroform. To this was added an equivalent amount of bromine (2.8 g.) dissolved in 20 ml. of chloroform. Both solutions had been chilled in ice. The mixture was heated on a steam bath to remove the chloroform. (If, however, the mixture was held at ice-salt temperatures a precipitate of the presumed tribromide X was obtained; (m.p. 160–165°). The resulting oil was distilled. The distillate (180°/0.5–1 mm.) solidified and upon recrystallization from methanol, 4-bromo-*o*-terphenyl (2.5 g.; 46%) was obtained; m.p. 89–90.5°; λ_{max} 237 mμ (ϵ 3.3 × 10^4).

Anal. Calcd. for $C_{18}H_{13}Br$: C, 69.94; H, 4.24. Found: C, 69.96; H, 4.52.

Quinque[2.4.3]phenyl, (VII). The lithium derivative from 4-bromo-*o*-terphenyl (2 g.) was prepared by the interchange reaction with *n*-butyllithium in ether. To this solution 3-phenyl-2-cyclohexenone (2.2 g.) dissolved in ether was added. The addition complex was decomposed with dilute sulfuric acid and the ether layer was submitted to steam distillation. The residue in the steam pot was extracted with ether. The ether was evaporated and the resulting crude diene was dissolved in a minimum of *p*-cymene to which was added a small amount of palladium charcoal. This mixture was heated under reflux until the evolution of hydrogen ceased (about 0.5 hr.) and was then filtered. *p*-Cymene was removed by distillation and the residue was dissolved in petroleum ether (b.p. 60–80°) and passed through a chromatographic column of alumina. The earlier fractions contained residual *p*-cymene and some *o*-terphenyl. The subsequent eluant contained the quinquephenyl which upon concentration and chilling crystallized. The material was recrystallized from petroleum ether (b.p. 60–80°); yield: 1 g. (40%); m.p. 119.5–120°. No depression of melting point on admixture with earlier prepared sample.

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.46; H, 6.07.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Electrolysis of Bromobenzene in Pyridine Solutions[1]

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An investigation of the electrolysis of bromobenzene in pyridine solutions has been carried out between magnesium electrodes and also between a magnesium anode and a platinum cathode. Products isolated from the anolyte included benzene, 4,4′-dipyridyl, and the three isomeric phenylpyridines, with 4-phenylpyridine being the predominant isomer. Evidence is presented in support of mechanisms of reaction involving unipositive magnesium and phenyl radicals as intermediates.

When platinum was employed as cathode, benzene and the three isomeric phenylpyridines were obtained from the catholyte. The distribution of phenylpyridines corresponded very closely to that which results when pyridine is caused to react with a variety of reagents known to give rise to phenyl radicals. However, with a magnesium cathode the situation was much more complex. The electrode was corroded to a significant extent, and of the isomeric phenylpyridines isolated from the catholyte, the 4-isomer was predominant. Furthermore, 4,4′-dipyridyl was also found. The results indicate that here, as in the anolyte, the formation of unipositive magnesium exerts a profound influence on the course of reaction.

The results of this investigation and their interpretation, taken with previous observations, suggest a mechanism for the formation of Grignard reagents which involves a chain reaction with hydrocarbon radicals and unipositive magnesium serving as chain carriers.

Evidence has been presented in previous communications from this laboratory[2] that lower valent magnesium and aluminum species are formed as intermediates in the anodic oxidation of the metals in various media. These lower valent forms of the elements are highly reactive and readily give up electrons either to the anode or to an oxidant present in solution. It has been shown that in the presence of bromobenzene in pyridine solutions containing suitable electrolytes both magnesium and aluminum enter solution with initial mean valence numbers significantly lower than their characteristic values.[3] Since it is well known that the reaction of bromobenzene with magnesium results in the formation of a Grignard reagent, it was thought that the "anodic reduction" of bromobenzene in sodium iodide–pyridine solutions between magnesium electrodes might provide valuable evidence regarding the mechanism of the formation of Grignard reagents. This would be true particularly if the products formed in the anolyte were capable of attacking massive mag-

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[1] Sponsored by the Office of Ordnance Research, U.S. Army.

[2] See T. T. Tsai, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.,* **82**, 3326 (1960) and papers cited therein.

[3] M. D. Rausch, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.,* **77**, 2093 (1955).