aromatized compound. This septiphenyl was identical with the septiphenyl VIII (R = 4-*m*-terphenyl).

The above diketone XIX, 5 g., dissolved in toluene was added to the Grignard reagent prepared from 14 g. of 3-xenyl bromide and 1.46 g. of magnesium in 25 ml. of ether. The product was treated as above. The stem-pot residue was isolated and recrystallized from dimethyl sulfoxide; yield 5.9 g. (71%), m.p. 247–250°, ϵ_{max}(ethoxyethanol) 8.0 × 10^4 (265 mμ) and an inflection at 325 mμ.

Anal. Calcd. for $C_{54}H_{42}$: C, 93.87; H, 6.13. Found: C, 93.50; H, 6.21.

Aromatization was effected in a large amount of *p*-cymene with 10% palladium–charcoal in the usual manner. The product was recrystallized from dimethyl sulfoxide; m.p. 249–250°, ϵ_{max}(ethoxyethanol) 10 × 10^4 (257 mμ).

Anal. Calcd. for $C_{54}H_{38}$: C, 94.42; H, 5.58. Found: C, 94.24; H, 5.56.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND, COLLEGE PARK, MD.]

Branched Polyphenyls

BY G. FORREST WOODS, JOHN C. OPPELT AND ROBERT B. ISAACSON

RECEIVED OCTOBER 30, 1959

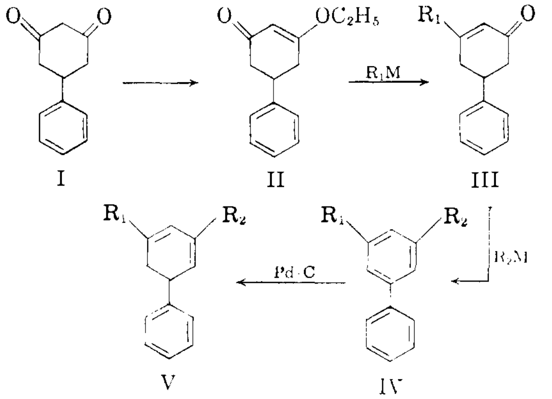
Two methods have been developed and employed for the synthesis of several branched polyphenyls.

Previous papers[1] from this Laboratory have dealt with the linear or normal polyphenyls up to the noviphenyls. In this paper, the synthesis and properties of several examples of branched polyphenyls[2] are reported.

Of the possible methods of synthesis of branched polyphenyls we have explored the reaction of cyclohexenones with aryl Grignard reagents or lithium derivatives. The branching can be a consequence of a structural feature of the ketone (as shown below) or in the organometallic (as is indicated later in the formula sequence I → V).

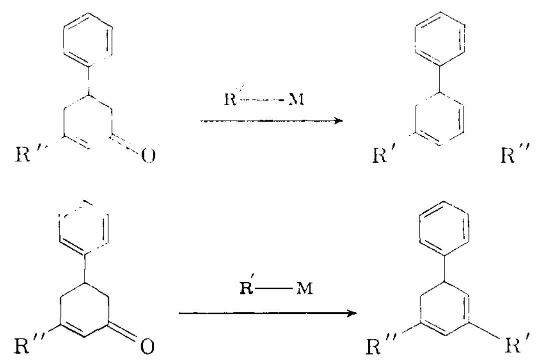
The diketone I[3] is converted readily to its enol ether II[4]; and the cyclohexenones III which were prepared by the reaction of II with organometallic reagents are listed in Table I along with certain physical properties.

Treatment of the disubstituted cyclohexenones with the appropriate Grignard reagent or organolithium compound provided trisubstituted cyclohexadienes IV.



IVa, R_1 = R_2 = phenyl ⟶ V_a
b, R_1 = phenyl, R_2 = *p*-xenyl ⟶ V_b
c, R_1 = phenyl, R_2 = *m*-xenyl ⟶ V_c
d, R_1 = phenyl, R_2 = *o*-xenyl ⟶ V_d
e, R_1 = *o*-xenyl, R_2 = *p*-xenyl ⟶ V_e
f, R_1 = R_2 = *p*-xenyl ⟶ V_f

Certain of the dienes could not be induced to crystallize. We believe that certain factors contribute to this: (1) products with *meta* or *ortho* linkages are always more difficult to obtain in a crystalline state. (2) Although we have written a precise dienic structure, no evidence has been obtained which excludes the possibility of rearrangement of ethylenic links. Indeed, alternate preparations of a given diene usually seem to lead to a product of the same composition instead of dienic isomers as shown



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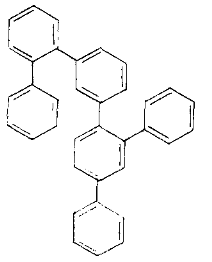
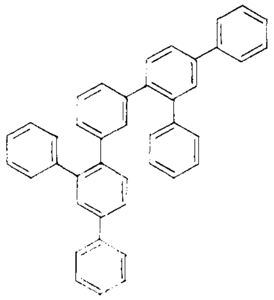
[1] G. F. Woods, D. D. Centola, H. E. Ruskie and C. D. Miller, THIS JOURNAL, **82**, 5227 (1960).

[2] In order to designate the mode of linkages of the aromatic nuclei in the polyphenyls and to locate a substituent on a nucleus in the polyphenyl chain it is recommended that: (1) Arabic numerals be employed to designate the mode (*o*-, *m*-, *p*-) of linkage of the aromatic nuclei; and (2) that Roman numerals be employed to designate the particular ring to which a substituent is attached. It is also suggested that Arabic numerals be used to indicate the position of a substituent on a particular nucleus.

The following two examples make obvious the application of these recommendations which are employed in this and subsequent manuscripts.





II-Phenyl-[3]-quinque[4,3,2]phenyl

II-Phenyl-[3]-
IV-Phenyl-[2]-quinque[4,3,4]phenyl

[3] D. Vorlander, *Ber.*, **27**, 2053 (1894); Q. Michael and P. C. Freer, *J. prakt. Chem.*, *II*, **43**, 390 (1891).

[4] R. L. Frank and H. K. Hall, THIS JOURNAL, **72**, 1645 (1950).

TABLE I

PROPERTIES OF DISUBSTITUTED CYCLOHEXENONES

Ketones III	R_1M	M.p., °C.	Isooctane λ_{max}, mμ	$\epsilon_{max} \times 10^{-4}$	Yield, %	Formula	Carbon, %		Hydrogen, %	
							Calcd.	Found	Calcd.	Found
VI[a]	Phenylmagnesium bromide	82–83	274	1.9	40	$C_{18}H_{16}O$	87.06	87.15	6.50	6.35
VII	4-Xenyllithium	149–151	300	3.1	45	$C_{24}H_{20}O$	88.85	89.15	6.21	6.07
VIII	3-Xenylmagnesium bromide	105–106	254	3.1	54	$C_{24}H_{20}O$	88.85	88.79	6.21	5.87
IX[b]	2-Xenylmagnesium iodide	110–111	238	2.4	44	$C_{24}H_{20}O$	88.85	88.97	6.21	5.78

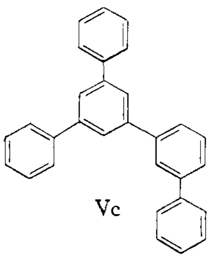
[a] Melting point reported: 82–83°, 83°; E. Knoevenagel and A. Erler, *Ber.*, **36**, 2133 (1903); E. P. Kohler, *Am. Chem. J.*, **37**, 386 (1907); the oxime melted at 166–168°; lit. (E. P. Kohler): 163°. *Anal.* Calcd. for $C_{18}H_{17}NO$: C, 82.09; H, 6.51. Found: C, 81.90; H, 6.72. [b] The oxime melted at 176–178°. *Anal.* Calcd. for $C_{24}H_{21}NO$: C, 84.90; H, 6.20. Found: C, 84.34; H, 6.05.

Thus it is possible that IVb, IVc, IVd and IVe are mixtures of dienic isomers. (3) All of the dienes tend to lose hydrogen (and aromatize) by reaction probably with atmospheric oxygen resulting in further complexities.

The dienes IV were readily aromatized to V by means of bromine addition–hydrogen bromide elimination or by dehydrogenation with palladium-on-charcoal in the usual manner.

Compound Va (1,3,5-triphenylbenzene) is of key importance. Since there is no method at present of proving structures of the polyphenyls, it was essential that a previously described substance, prepared by an alternate procedure, be obtained from the mode of synthesis described in this work.

Compound Vc whose preparation was attempted by aromatization with bromine or palladium-on-charcoal could not be induced to crystallize. We have encountered similar crystallization difficulties with other compounds containing the *meta* link.

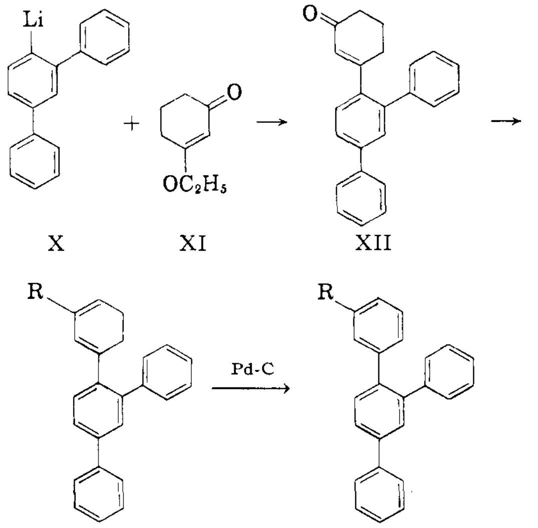


Vc

Another method of obtaining branched polyphenyls depends on more complex aryllithium derivatives. For this purpose the lithium derivative (X) prepared from 4′-bromo-*m*-terphenyl was treated in the manner shown. It will be noted that many of the substances prepared by the two synthetic routes are isomeric.

Experimental

Ethyl Enol Ether of 5-Phenyldihydroresorcinol (II).—5-Phenyldihydroresorcinol (250 g.) was heated under reflux with a mixture of benzene (1500 ml.), absolute ethanol (250 ml.) and 5 g. of *p*-toluenesulfonic acid.[4] A Dean–Stark trap was employed to collect the water evolved. After evolution of water had ceased, the mixture was cooled, shaken with dilute sodium carbonate solution and finally with water. The organic layer was dried and the solvent removed on a concentrator under reduced pressure. The product was dissolved in anhydrous ether and the resulting mixture cooled in a Dry Ice–acetone-bath; with much scratching and stirring, solid precipitated which was recrystallized several times to yield the enol ether, 230 g. (80%), melting at 43°, lit.[5] 43°.



X XI XII

XIIIa, R = phenyl
b, R = *p*-xenyl
c, R = *m*-xenyl
d, R = *o*-xenyl

Ketones VI, VII, VIII and IX.—To an excess of organometallic reagent (phenylmagnesium bromide, 4-xenyllithium, 3- and 2-xenylmagnesium bromide) in ether was added a solution of the enol ether dissolved in anhydrous ether. After the addition was complete, the reaction medium was acidified with dilute sulfuric acid and the aqueous layer rejected. The ethereal layer was steam distilled from a dilute sulfuric acid medium until essentially all volatile organic material was removed. The residue was extracted with ether and the ether solution concentrated and cooled whereupon crystalline material was formed. The physical data and yields are given in Table I.

1,3,5-Triphenylbenzene (Va) and Its Precursor Diene IVa.—An ethereal solution of 3,5-diphenyl-2-cyclohexenone (2.63 g. of VI) was added to an ethereal solution of phenylmagnesium bromide prepared from 0.02 mole of bromobenzene and magnesium. The addition complex was decomposed with cold dilute sulfuric acid. The ether layer was washed and dried. Approximately 90% of the ether was removed and upon chilling the residue in an ice-bath white crystalline IVa precipitated which was recrystallized from 95% ethanol; yield 2.82 g. (86%), m.p. 110–111°, lit.[5] m.p. 111°; λ_{max} (isoöctane) 253.5 mμ (ϵ 2.7 × 10^4), 316.5 mμ (1.0 × 10^4).

Anal. Calcd. for $C_{24}H_{20}$: C, 93.45; H, 6.54. Found. C, 93.44; H, 6.60.

Approximately 0.5 g. of the diene was dissolved in a minimum of *p*-cymene containing a small amount of 10% palladium-on-charcoal and the whole heated under reflux for 1 hour. The catalyst was removed by filtration of the still warm solution. A small quantity of ethanol was added and the solution chilled. White crystalline 1,3,5-triphenylbenzene precipitate which was recrystallized from benzene–ethanol (1:1); yield 0.45 g. (95%), m.p. 171–172°, lit.[6] m.p. 170–171°, λ_{max} (isoöctane) 250 mμ (ϵ 6.8 × 10^4).

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(5) C. M. Suter and P. G. Smith, THIS JOURNAL, **61**, 166 (1939).

(6) E. P. Kohler *Am. Chem. J.*, **37**, 386 (1907).

Anal. Calcd. for $C_{24}H_{18}$: C, 94.08; H, 5.92; mol. wt., 306. Found: C, 93.99; H, 5.98; mol. wt. (cryoscopic), 310.5.[7]

II-Phenyl-[5]-quater[3,4]phenyl (Vb) and Its Dienic Precursor (IVb).—The diene XI was prepared by two methods: (a) the reaction of 3,5-diphenyl-2-cyclohexenone with a slight excess of 4-xenyllithium (by direct reaction of 4-xenylbromide with lithium) in ether and (b) the reaction of 5-phenyl-3-(4-xenyl)-2-cyclohexenone with an excess of phenylmagnesium bromide in ether. In both instances the complex was decomposed with dilute sulfuric acid and the other layer submitted to steam distillation. The residue in the steam-pot was dissolved in ether. (The ether solution at this stage from (a) was filtered to remove a small quantity of *p*-quaterphenyl.) The ether layer was washed, dried, and concentrated. Upon addition of petroleum ether (60–80°) yellow crystalline diene precipitated which was recrystallized from ethanol to yield a white crystalline material; yield 55%, m.p. 158–160°, λ_{max} (isoöctane) 327 mμ (ϵ 3.1 × 10^4).

Anal. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 93.87; H, 6.47.

The aromatization of the diene was accomplished with palladium-on-charcoal in boiling *p*-cymene as described for 1,3,5-triphenylbenzene; yield 95%, m.p. 134–135°, λ_{max} (isoöctane) 262 mμ (ϵ 5.8 × 10^4, concn. 1.38 × 10^{-5} mole/l.); ϵ 6.2 × 10^4, concn. 2.93 × 10^{-5} mole/l.). (It has been shown for substances of this type that λ_{max} varies as a function of the concentration.)

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80; mol. wt., 382.5. Found: C, 94.45; H, 5.79; mol. wt. (cryoscopic), 396.

II-Phenyl-[5]-quater[3,2]phenyl (Vd).—5-Phenyl-3-(2-xenyl)-2-cyclohexenone (6.84 g. of IX) was treated with an excess of phenylmagnesium bromide in the usual manner. The complex was decomposed with dilute sulfuric acid, and steam distilled. Isolation of the product was effected as has been described above. The diene (6.2 g., 87%) IVd could not be induced to crystallize.

The impure diene (2.6 g.) was dissolved in 10 ml. of carbon tetrachloride and the solution chilled. A solution of bromine (1.10 g.) in 10 ml. of carbon tetrachloride was added until the color of bromine persisted. The resulting solution was heated to boil off the carbon tetrachloride which was replaced with ethanol. An oil formed which crystallized upon standing, and was recrystallized from ethanol–benzene (1.1); yield 65%, m.p. 119–120°; λ_{max} (isoöctane) 241 mμ (ϵ 6.8 × 10^4), 250 mμ (ϵ 6.7 × 10^4).

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.27; H, 5.50.

III-Phenyl-[5]-quinque[2,3,4]phenyl (Ve).—3-(2-Xenyl)-5-phenyl-2-cyclohexenone (ketone IX, 9.74 g., 0.03 mole) dissolved in tetrahydrofuran was added to an excess of 4-xenylmagnesium bromide prepared in tetrahydrofuran. The addition complex was decomposed with dilute sulfuric acid. The aqueous layer was rejected and the ether layer filtered to remove a small amount of *p*-quaterphenyl. The product was submitted to steam distillation and the oily steam-pot residue, 13.8 g. (95%), isolated. It could not be induced to crystallize.

This material was aromatized in carbon tetrachloride with bromine, as described earlier. After evaporation of most of the solvent, the residual oil was dissolved in a mixture of toluene–absolute ethanol, chilled and filtered. The resulting crystalline precipitate was recrystallized from absolute ethanol; yield 6.5 g. (47%), m.p. 115°. Upon continued heating above this melting point solidification occurred and remelting took place at 126–128°.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol. wt., 458.6. Found: C, 94.53; H, 5.70; mol. wt. (cryoscopic), 461.

III-Phenyl-[5]-quinque[4,3,4]phenyl (Vf) and Its Precursor Diene IVf.—5-Phenyl-3-(4-xenyl)-2-cyclohexenone (ketone VII, 6.48 g., 0.02 mole) was treated with excess 4-xenylmagnesium bromide in a manner described previously. After steam distillation, the steam-pot residue was cooled and the oily residue solidified. The solid was isolated by extraction with a large amount of ether. Removal of most of the ether resulted in precipitation of a yellow crystalline product. This product was dissolved in a mixture of benzene–petroleum ether (60–80°) and passed through a short column of alumina. Concentration of the solution which passed through the column, upon cooling, provided pale yellow diene IVf; yield 5.7 g. (62%), m.p. 168–170°, λ_{max}(isoöctane) 286 mμ (ϵ 5.3 × 10^4), inflection at 320 mμ.

Anal: Calcd. for $C_{36}H_{28}$: C, 93.87; H, 6.13. Found: C, 93.61; H, 6.10.

The diene was aromatized in carbon tetrachloride with bromine, as described earlier. Upon removal of excess carbon tetrachloride, crystalline material precipitated and was isolated by filtration. Recrystallization from toluene–ethanol yielded the aromatic hydrocarbon Vf in 40% over-all yield, m.p. 203–204°, λ_{max}(isoöctane) 279 mμ (ϵ 7.7 × 10^4).

Anal. Calcd. for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol. wt., 458.6. Found: C, 94.24; H, 5.68; mol. wt. (cryoscopic), 441.

Preparation of Ketone XII.—*n*-Butyllithium (123 ml. of 0.82 *N*) ether solution, 0.1 mole) was added dropwise to an ethereal solution of 4′-bromo-*m*-terphenyl[7] (20.5 g., 0.066 mole). The addition was carried out at 0° with stirring. After addition was complete, the mixture was stirred at room temperature for 0.5 hour and the enol ether of dihydroresorcinol (14.0 g., 0.1 mole), dissolved in ether, added slowly. The mixture was allowed to reflux for 1 hour after addition of the enol ether was completed. The addition complex was decomposed with cold dilute sulfuric acid. The organic layer was steam distilled from dilute sulfuric acid until little organic material could be detected in the steam distillate. The viscous yellow material remaining in the steam distillation flask was extracted with ether and washed successively with sodium bicarbonate and water. The ether layer was dried over magnesium sulfate. Upon concentration of the ethereal solution and cooling, a yellow precipitate was obtained. This was recrystallized from anhydrous ether; yield 10.0 g. (47%), m.p. 142°.

Anal. Calcd. for $C_{24}H_{20}O$: C, 88.84; H, 6.23. Found: C, 88.54; H, 6.21.

The 2,4-dinitrophenylhydrazone was prepared in the usual manner; m.p. 232°.

Anal. Calcd. for $C_{30}H_{24}N_4O_4$: C, 71.42; H, 4.80. Found; C, 71.42; H, 5.07.

Preparation of II-Phenyl-[3]-quater[4,3]phenyl (XIIIa).—Ketone XII (2.7 g., 0.0083 mole) dissolved in anhydrous ether–benzene (4:1) was added slowly to an ethereal solution of phenyllithium (12 ml. of 1.3 *N* solution, 0.016 mole). The mixture was stirred for several hours. The complex was decomposed with cold dilute sulfuric acid. The organic layer was diluted with ether and, after rejection of the water layer, was submitted to steam distillation from dilute sulfuric acid solution. The steam distillation was continued until no further organic material could be detected in the steam distillate. The viscous residue remaining in the distillation flask was extracted with ether and the ethereal layer washed several times with sodium bicarbonate and finally with water. The ethereal solution was dried over magnesium sulfate. Evaporation of the ether yielded a viscous yellow oil. Chromatography, employing an alumina column and petroleum ether (60–80°)–benzene (20:1) as the eluent, failed to yield a crystalline product. The oil was dissolved in *p*-cymene and heated under reflux with palladium-on-charcoal for 1 hour. The hot solution was filtered and excess *p*-cymene was removed by distillation. The resulting viscous material was passed through an alumina chromatographic column with petroleum ether (60–80°)–benzene (20:1) as the eluent. The early fractions contained non-adsorbed crystalline hydrocarbon material isolated by removal of most of the solvent, followed by chilling. This hydrocarbon was recrystallized from petroleum ether (30–60°); yield 0.9 g. (30% from ketone XII), m.p. 104–105°, λ_{max}(isoöctane) 248 mμ (ϵ 5.8 × 10^4), inflection at 267 mμ.

Anal. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80; mol. wt., 382.5. Found: C, 93.98; H, 5.94; mol. wt. (cryoscopic), 385.

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[7] Cryoscopic molecular weight determinations were made using *p*-terphenyl as solvent.

[8] L. Olgiatti, *Ber.*, **27**, 3387 (1894).

Preparation of II-Phenyl-[3]-quinque[4,3,4]phenyl (XIIIb).—A solution of 4-xenyllithium was prepared in the usual manner from 4.2 g. of *p*-bromobiphenyl (0.018 mole) and 0.28 g. of lithium metal (0.040 mole). Ketone XII (3.9 g., 0.012 mole), in 25 ml. of dry benzene, was added dropwise and the complex was decomposed with cold dilute sulfuric acid. The product was treated as described above for hydrocarbon XIIIa. Crystalline material was obtained at both the dienic and aromatic stage without the use of chromatography. The aromatic compound was recrystallized from isopropyl alcohol-benzene; yield 3.7 g. (68% from ketone XII), m.p. 182–184°, λ_{max}(isoöctane) 279 mμ (ϵ 5.6 × 10^4), 252 mμ (ϵ 4.1 × 10^4).

Anal. Calcd. for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol. wt., 458.6. Found: C, 94.42; H, 5.72; mol. wt. (cryoscopic), 468.

Preparation of 3-Xenyl Bromide.—The method used was essentially that of Huber, *et al.*[9] A slight modification of Huber's procedure afforded 3-xenyl bromide of high purity. Chromatography, employing an alumina column, followed by a second distillation produced a purer product. The 3-xenyl bromide, which had previously been reported as a liquid, was recrystallized from petroleum ether (30–60°); m.p. 9°. (Use of this 3-xenyl bromide did not, however, alleviate the problem of crystallization difficulties with polyphenyls containing *meta* links.)

Preparation of II-Phenyl-[3]-quinque[4,3,3]phenyl (XIIIc) and Its Dienic Precursor.—Ketone XII (3.24 g., 0.01 mole) was added slowly in dry benzene to a solution of 3-xenylmagnesium bromide prepared in the usual manner from 4.7 g. of 3-xenyl bromide (0.02 mole) and 0.5 g. of magnesium metal (0.02 mole). The addition complex was decomposed and the reaction product treated as described previously for hydrocarbon XIIIa. The diene was induced to crystallize in an ethanol–benzene mixture. It was recrystallized from ethanol–benzene (1:1) to a pale yellow solid; yield 3.0 g. (65%), m.p. 132–134°, λ_{max}(isoöctane) 248 mμ, inflections at 275 and 320 mμ.

Anal. Calcd. for $C_{36}H_{28}$: C, 93.88; H, 6.12. Found: C, 93.69; H, 5.84.

One gram of the diene in *p*-cymene was refluxed with palladium-on-charcoal. The aromatic product was treated in a manner similar to that employed in the synthesis of hydrocarbon XIIIa. The aromatic hydrocarbon was recrystallized from petroleum ether (60–80°)–benzene (1:1); yield 0.92 g. (99% from diene, 64% from ketone), m.p. 145–146°, λ_{max}(isoöctane) 248 mμ (ϵ 6.4 × 10^4).

Anal. Calcd. for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol. wt., 458.6. Found: C, 94.12; H, 5.57; mol. wt. (cryoscopic), 470.

Preparation of II-Phenyl-[3]-quinque[4,3,2]phenyl (XIIId).—Ketone XII (3.9 g., 0.012 mole), in dry benzene, was added slowly to an ethereal solution of 2-xenylmagnesium iodide that was prepared from 70 g. (0.025 mole) of 2-xenyl iodide and 0.6 g. of magnesium metal (0.025 mole). The complex was decomposed and the product treated as described for XIIIa. The crude diene was refluxed for 1 hour in *p*-cymene with palladium-on-charcoal. The product was treated in a manner similar to that described for hydrocarbon XIIIa. The polyphenyl was recrystallized from petroleum ether (60–80°)–benzene (1:1); yield 2.3 g. (42% from ketone XII), m.p. 172–174°, λ_{max}(isoöctane) 242 mμ (ϵ 4.8 × 10^4), inflection at 267 mμ.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.28; H, 5.72; mol. wt., 458.6. Found: C, 94.24; H, 5.90; mol. wt., (cryoscopic), 465.

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

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(9) W. F. Huber, M. Renoll, A. G. Rossow and D. T. Mowry, THIS JOURNAL, **68**, 1111 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

The Baeyer–Villiger Oxidation of Bicyclic Ketones

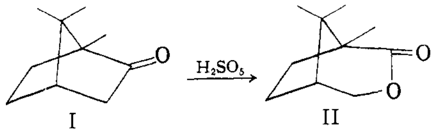
BY JERROLD MEINWALD[1] AND ELLIOTT FRAUENGLASS[2]

RECEIVED MARCH 5, 1960

The peracetic acid oxidation of bicyclo[2,2,1]heptanone-2 was carried out in buffered medium and in the presence of a strong acid catalyst. The primary product, in each case, was found to be the lactone of *cis*-3-hydroxycyclopentylacetic acid, corresponding to migration of the bridgehead carbon atom. The structure of this product was proved by direct comparison with an independently synthesized sample. The isomeric lactone, derived from *cis*-3-hydroxymethylcyclopentanecarboxylic acid, was also synthesized by an unambiguous route, and was not found in the Baeyer–Villiger reaction product. The oxidation of bicyclo[2,2,2]octanone was found to give rise to *cis*-4-hydroxycyclohexylacetic acid lactone, while bicyclo-[2,2,2]octen-5-one-2 suffered attack at the carbonyl group rather than at the double bond yielding a rearranged lactone derived from 2-hydroxycyclohexen-3-ylacetic acid. The factors determining the migrating group in these and related Baeyer–Villiger reactions are discussed briefly.

Introduction.—In 1899, Baeyer and Villiger reported the first examples of the peracid oxidation of ketones to esters or lactones.[3] Since that time this type of oxidation has found a wide variety of important synthetic and degradative applications.[4] Thus, peracids have been used to synthesize a variety of steroid and terpene lactones, as well as lactones involving medium and large rings which are virtually unobtainable by any other means.

Although the general mechanistic features of this oxidative rearrangement are understood,[4] the original observation of Baeyer and Villiger that persulfuric acid transforms camphor (I) into α-campholide (II) (see eq. 1) has been difficult to understand since this reaction course implies that the migration of a primary group (methylene) has taken precedence over the migration of a tertiary group (the bridgehead carbon). This implication, which is hard to reconcile with the more generally observed rule that in an unsymmetrical ketone the group which can better accommodate the positive charge will migrate, has been rationalized by Murray, Johnson, Pederson and Ott on the basis of a



I II (1)

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[1] Fellow of the Alfred P. Sloan Foundation.

[2] Monsanto Fellow, 1959.

[3] A. Baeyer and V. Villiger, *Ber.*, **32**, 3625 (1899).

[4] For a convenient survey of this reaction see the review by C. H. Hassall in R. Adams, "Organic Reactions," Vol. 9, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 73.