solution. Extraction with benzene gave 3.2 g. (8.7%) of light yellow crystals of pure 2,4-dinitrophenol, m. p. 113–114°.

Basic Phenylmercuric Nitrate from Phenylmercuric Acetate.—One hundred grams of powdered phenylmercuric acetate was added gradually to a solution of 125 ml. of concentrated ammonium hydroxide (28%) in 400 ml. of water heated on a steam cone. An additional 20 ml. of concentrated ammonia was added, after which most of the solid had dissolved. The solution was heated to boiling and filtered directly into 75 ml. of vigorously stirred 70% nitric acid. An additional 5 ml. of 70% nitric acid was introduced into the mixture, which was then boiled for one minute, cooled to 5°, and filtered. The solid, after being washed with ice water and dried, consisted of 73.3 g. (77.5%) of white basic phenylmercuric nitrate, m. p. 181–182° (dec.).

Summary

Studies of some of the intermediate stages in the oxynitration of benzene are described. Basic phenylmercuric nitrate was isolated from an oxynitration reaction mixture. Phenylmercuric salts were shown to react with nitric acid to produce 2,4-dinitrophenol. The mercuration of benzene in dilute nitric acid was studied. Nitrosobenzene was oxynitrated without the use of mercuric nitrate as a catalyst. The stoichiometric consequences of Darzens' proposed mechanism for oxynitration were investigated. The fate of some other possible intermediates was studied under typical oxynitration conditions. A convenient procedure was developed for the conversion of phenylmercuric acetate into basic phenylmercuric nitrate.

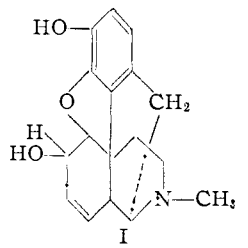
PHILADELPHIA, PA. RECEIVED NOVEMBER 13, 1946

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Angular Aryl Group. 10-Phenyldecahydroquinoline and 9-Phenyldecalin

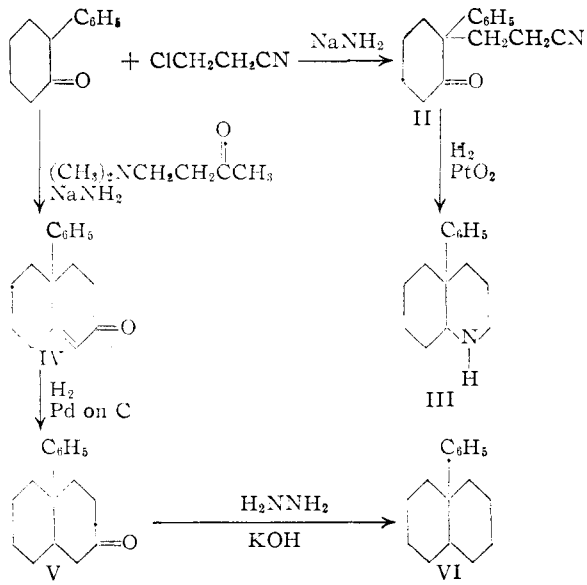
BY VIRGIL BOEKELHEIDE[1]

Although considerable research has been done on compounds with fused rings having a methyl group at the angular position, relatively few compounds have been synthesized having an angular group other than methyl.[2] It might be thought that there is insufficient free space at the angular position for a large group. Yet this is not borne out by the experimental work that has been done. Thus Allen and VanAllan were able to establish that treatment of methylanhydroacetonebenzil with acid yielded a compound having an angular phenyl group.[3] Also Allen, Bell, Clark and Jones have reported some reduced naphthoquinones having an angular phenyl group.[4] The angular aryl group is important in regard to the structures which have been proposed for morphine[5] and for strychnine.[6] Thus the Gulland and Robinson structure for morphine, as shown below in formula I, may be regarded as an octahydroisoquinoline derivative having an angular aryl group. The work to be described was carried out for the purpose of preparing some model compounds of relatively simple structure which would have an angular aryl group.



I

The synthesis of 10-phenyldecahydroquinoline was readily accomplished in fair yield by the scheme shown below. The reaction of 2-phenylcyclohexanone with β-chloropropionitrile in the presence of sodium amide gave 2-(β-cyanoethyl)-2-phenylcyclohexanone, II. The location of the cyanoethyl group was established by the reaction of II with benzaldehyde. The formation of the



(1) Present address: Department of Chemistry, University of Rochester, Rochester, New York.

(2) Examples of angular groups other than methyl that have been reported in the literature include the following: ethyl (Ghosh and Robinson, *J. Chem. Soc.*, 506 (1944)), allyl, (Grewe, *Ber.*, **76**, 1072 (1943)), dichloromethyl (Woodward, THIS JOURNAL, **62**, 1208 (1940)), and carbethoxyl (Fieser and Holmes, *ibid.*, **60**, 2548 (1938)).

(3) C. F. H. Allen and J. VanAllan, THIS JOURNAL, **64**, 1260 (1942); *J. Org. Chem.*, **10**, 333 (1945).

(4) Allen, Bell, Clark and Jones, THIS JOURNAL, **66**, 1617 (1944).

(5) Gulland and Robinson, *Mem. Proc. Manchester Lit. & Phil. Soc.*, **69**, 79 (1925).

(6) Briggs, Openshaw, and Robinson, *J. Chem. Soc.*, 903 (1946); Prelog and Metzler, *Helv. Chim. Acta*, **29**, 1163 (1946).

benzal derivative in almost quantitative yield is proof of the presence of a methylene group adjacent to the carbonyl group. Catalytic reduction of II using platinum oxide as catalyst resulted in ring closure and the formation of the desired 10-phenyldecahydroquinoline, III.

The synthesis of 9-phenyldecalin was carried out in a similar manner. The reaction of 2-phenylcyclohexanone with 4-dimethylaminobutanone-2 gave 9-phenyl-$\Delta^{4,10}$-octalone-3, IV. Catalytic hydrogenation of IV using palladium on charcoal yielded 9-phenyldecalone-3, V, which was further reduced by treatment with hydrazine hydrate and alkali to give the desired 9-phenyldecalin, VI.

In view of the synthesis of 10-phenyldecahydroquinoline and also in view of the previous work[7,8] on the alkylation of substituted cyclohexanones, it has been assumed that the correct structure for VI is that of 9-phenyldecalin. It is recognized that unusual rearrangements of the phenyl group have been reported.[9] However, under the mild conditions used for the synthesis of III and IV it is quite unlikely that migration of the phenyl group would have occurred.

The synthesis of the previously unknown 1-phenyldecalin was carried out in order to compare its properties with those of VI. The isomer of 1-phenyldecalin, which was prepared, was obtained by treating *cis*-1-decalone with phenylmagnesium bromide. The resulting 1-phenyloctalin was then hydrogenated to give 1-phenyldecalin. It was found, as expected, that VI had a higher melting point and a higher refractive index than did the 1-phenyldecalin.

Further investigations of VI and related compounds, particularly dehydrogenation studies, are now in progress.

Experimental[10,11]

2-(β-Cyanoethyl)-2-phenylcyclohexanone, II.—A prepared solution consisting of 2-phenylcyclohexanone (26.0 g., 0.15 mole), benzene (70 ml.) and ether (100 ml.) was added dropwise with stirring to a mixture of sodium amide[12] (6.8 g., 0.20 mole) and dry ether (125 ml.). After the addition was complete the mixture was boiled under reflux until ammonia was no longer evolved. Then a solution of β-chloropropionitrile (17.8 g., 0.20 mole) in ether (125 ml.) was slowly added and the resulting mixture was boiled gently under reflux for twelve hours. At the conclusion of the reaction water (250 ml.) was added. The ether layer was separated, washed with water, and dried. After the ether had been removed *in vacuo* the residue was distilled. There was obtained 21.0 g. (63%) of a colorless oil; b. p. 146–147° (0.5 mm.); $n^{20}D$ 1.5438. A micro molecular weight determination indicated a molecular weight of 223. The calculated molecular weight is 227.

Anal. Calcd. for $C_{15}H_{17}NO$: C, 79.27; H, 7.55. Found: C, 79.32; H, 7.42.

The **benzal derivative** of II was prepared by treating a solution of the ketone (3.0 g.) in alcohol (20 ml.) with a 15% sodium hydroxide solution (8 ml.) followed by addition of benzaldehyde (2.5 g.). The heavy oil, which separated, crystallized after standing at room temperature for six days. The benzal derivative was crystallized from ethanol and there was obtained 4.0 g. (95%) of fine white needles, m. p. 83–84°.

Anal. Calcd. for $C_{22}H_{21}NO$: C, 83.78; H, 6.71. Found: C, 83.65; H, 6.63.

The **benzal derivative of 2-phenylcyclohexanone** was prepared in a similar manner for purposes of comparison. The benzal derivative of 2-phenylcyclohexanone was obtained from ethanol as white needles, m. p. 89–90°.

Anal. Calcd. for $C_{19}H_{18}O$: C, 86.98; H, 6.92. Found: C, 86.90; H, 7.00.

10-Phenyldecahydroquinoline, III.—A solution of 2-(β-cyanoethyl)-2-phenylcyclohexanone (15.0 g., 0.067 mole) in absolute alcohol (150 ml.) was added to a reduced mixture of platinum oxide (0.20 g.) and absolute alcohol (50 ml.). The mixture was shaken under a pressure of three atmospheres of hydrogen for thirty-six hours. Then the catalyst was removed by filtration, the solvent was removed *in vacuo*, and the residue was distilled. There was obtained 6.0 g. (40%) of a colorless oil; b. p. 112° (0.7 mm.); $n^{20}D$ 1.5565. A micro molecular weight determination indicated a molecular weight of 218. The calculated molecular weight is 215.

Anal. Calcd. for $C_{15}H_{21}N$: C, 83.67; H, 9.83. Found: C, 83.76; H, 9.56.

The **picrate** of III was readily obtained by treatment of III with a solution of picric acid in alcohol. The crystals, which were obtained from alcohol, became liquid at 118°, resolidified, and melted at 155–157°. This behavior and the analysis indicated that the picrate had a molecule of alcohol of crystallization.

Anal. Calcd. for $C_{21}H_{24}N_4O_7 + C_2H_6O$: C, 56.14; H, 6.14. Found: C, 56.32; H, 6.04.

9-Phenyl-$\Delta^{4,10}$-octalone-3, IV.—A prepared solution consisting of 2-phenylcyclohexanone (26.0 g., 0.15 mole), benzene (70 ml.) and ether (100 ml.) was added dropwise with stirring to a mixture of sodium amide (6.8 g., 0.20 mole) in dry ether (125 ml.). After the addition was complete the mixture was boiled under reflux until ammonia was no longer evolved. Then a solution of 4-dimethylaminobutanone-2[13] (24.0 g., 0.20 mole) in ether (125 ml.) was slowly added, and the resulting mixture was boiled gently under reflux for twelve hours. At the conclusion of the reaction water (250 ml.) was added. The ether layer was separated, washed with water, and dried. After the ether had been removed *in vacuo* the residue was distilled. In addition to a low boiling fraction consisting of 2-phenylcyclohexanone (10 g.) there was obtained 9.0 g. (42% yield based on unrecovered ketone) of a viscous water-white oil; b. p. 136–140° (0.5 mm.); $n^{20}D$ 1.5820.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.01. Found: C, 84.96; H, 8.18.

The **semicarbazone** of IV was prepared readily and was obtained after crystallization from aqueous ethanol as hard white crystals, m. p. 230–232° (dec.).

Anal. Calcd. for $C_{17}H_{21}N_3O$: C, 72.05; H, 7.47. Found: C, 71.78; H, 7.51.

9-Phenyldecalone-3, V.—A solution of IV (11.3 g., 0.050 mole) in absolute alcohol (60 ml.) was shaken with 1 g. of 10% palladium-on-charcoal catalyst under a pressure of three atmospheres of hydrogen. Hydrogenation was complete in about two hours. The catalyst was then removed by filtration and the solvent was removed *in vacuo*. Distillation of the residue yielded 7.5 g. (66%) of a colorless oil; b. p. 128–130° (0.4 mm.); $n^{20}D$ 1.5590. On standing the oil crystallized as a white solid; m. p. 83–86°.

(7) du Feu, McQuillin and Robinson, *J. Chem. Soc.*, 53 (1937).

(8) Newman and Farbman, THIS JOURNAL, **66**, 1551 (1944).

(9) C. F. H. Allen and J. VanAllan, *ibid.*, **65**, 1384 (1942); *ibid.*, **66**, 7 (1944).

(10) The author wishes to thank Dr. L. K. Nash for his kindness in carrying out the micro molecular weight determinations. The method employed will be reported separately by Dr. Nash.

(11) Analyses by Miss Theta Spoor.

(12) Vaughn and Niewland, THIS JOURNAL, **56**, 2120 (1934).

(13) Mannich, *Arch. Pharm.*, **255**, 266 (1917).

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.12; H, 8.83. Found: C, 84.32; H, 9.28.

The **semicarbazone** of V readily was prepared and was obtained after crystallization from aqueous ethanol as flat white crystals, m. p. 222°.

Anal. Calcd. for $C_{17}H_{23}N_3O$: C, 71.55; H, 8.12. Found: C, 71.81; H, 8.31.

A mixture of the semicarbazone of V and the semicarbazone of IV melted below 200°.

9-Phenyldecalin, VI.—The reduction of V was carried out according to a method worked out by Baker.[14] A solution of V (6.0 g., 0.027 mole) in absolute alcohol (15 ml.) was boiled with 85% hydrazine hydrate (4 ml.) for four hours. The volatile material was removed and powdered potassium hydroxide (13 g.) was added. The flask containing the reaction mixture was then placed in a heating bath and the temperature was raised slowly. Nitrogen evolution, which began at 130°, was complete when the bath temperature reached 230°. When the flask had cooled, water was added and the organic layer was separated by benzene extraction. The benzene was removed and the residue distilled. There was obtained 4.0 g. (70%) of a colorless oil; b. p. 97–98° (0.3 mm.); $n^{20}D$ 1.5532. On standing the oil crystallized to a white solid, m. p. 52–53°.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.41; H, 10.44.

The **sulfonamide derivative** of VI was prepared according to the method of Huntress and Carten.[15] It was obtained by crystallization from aqueous ethanol as fluffy, white plates; m. p. 161–162°.

Anal. Calcd. for $C_{16}H_{23}NO_2S$: C, 65.50; H, 7.90. Found: C, 65.56; H, 7.94.

1-Phenyloctalin.—Decalone-1 (40 g., 0.26 mole), prepared by the chromic acid oxidation[16] of decalol-1,[17] was dissolved in ether (100 ml.). The ether solution was then added dropwise to a 3 *M* phenylmagnesium bromide solution (100 ml.). The reaction mixture was boiled under reflux for twenty minutes and was then hydrolyzed by slowly adding a dilute iced solution of hydrochloric acid. The ether layer was separated and the ether removed. The residual oil was boiled under reflux with 25 ml. of a 20% solution of sulfuric acid for two hours. The organic layer was then separated and distilled. There was obtained 24.0 g. (46%) of a colorless oil; b. p. 92–95° (0.1 mm.); $n^{20}D$ 1.5610.

Anal. Calcd. for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.33; H, 9.73.

1-Phenyldecalin.—The 1-phenyloctalin (18 g.) was shaken with 1 g. of 10% palladium-on-charcoal catalyst under a pressure of three atmospheres of hydrogen. Hydrogenation was complete after twenty-four hours. Distillation of the product gave 16 g. (90%) of a colorless oil; b. p. 103–104° (0.3 mm.); $n^{20}D$ 1.5420.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.89; H, 10.51.

The **sulfonamide** derivative of 1-phenyldecalin was prepared as before and was obtained, after crystallization from aqueous ethanol, as hard white plates, m. p. 154–158°.

Anal. Calcd. for $C_{16}H_{23}NO_2S$: C, 65.50; H, 7.90. Found: C, 65.37; H, 7.82.

A mixture of the sulfonamide of VI and the sulfonamide of 1-phenyldecalin was found to melt at 115–125°.

(14) B. R. Baker, Doctoral Dissertation, University of Illinois, 1940.

(15) Huntress and Carten, THIS JOURNAL, **62**, 511 (1940).

(16) This was carried out according to the procedure used for the oxidation of 3-methoxycyclohexanol-1 by Marvel and Walton, *J. Org. Chem.*, **7**, 88 (1942).

(17) Musser and Adkins, THIS JOURNAL, **60**, 664 (1938).

Summary

It has been shown that compounds having an angular aryl group can be synthesized without great difficulty. The synthesis of 10-phenyldecahydroquinoline and of 9-phenyldecalin is described.

URBANA, ILLINOIS RECEIVED JUNE 11, 1946

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Stobbe Condensation with Methyl *p*-Tolyl Ketone. A Synthesis of Cadalene

BY WILLIAM S. JOHNSON AND A. RUSSELL JONES[1]

In previous communications[2] we described a method involving the use of the Stobbe condensation for the introduction of a propionic acid side-chain at the site of the carbonyl group of a ketone. When applied to 2-acetylnaphthalene, this chain-lengthening process gave rise to a useful intermediate for the synthesis of 1,4-dimethylphenanthrene.[2a] In the present work the chain-lengthening process has been applied similarly to methyl *p*-tolyl ketone, I, and the product has been employed in a new synthesis of cadalene, VI.

Cadalene has been synthesized previously by various schemes involving from seven to eleven steps.[3] The highest over-all yield reported was about 3%. In the present synthesis cadalene was obtained as the picrate in about 25% over-all yield in six steps from methyl *p*-tolyl ketone. The reactions which were employed are indicated in the accompanying flow sheet. Although the intermediates II through V have been previously known, the present synthesis affords a new and easy source of these substances.

The condensation between the ketone I and diethyl succinate proceeded readily under the influence of potassium *t*-butoxide. The crude oily half ester thus was obtained in 90% yield, and undoubtedly consisted of a mixture of isomers. Decarbethoxylation with hydrobromic and acetic acid afforded crystalline γ-methyl-γ-*p*-tolylbutyrolactone, II, in 85% yield (75% after purification for reduction). This material was cleaved with dilute sodium hydroxide and the resulting aqueous solution of the salt of the hydroxy acid III was hydrogenated over copper–chromium oxide catalyst. The per cent. conversion to γ-*p*-

(1) Sterling-Winthrop Research Institute Fellow, 1946–1947.

(2) (a) Johnson, Goldman and Schneider, THIS JOURNAL, **67**, 1357 (1945); (b) W. S. Johnson, H. C. E. Johnson and Petersen, *ibid.*, **67**, 1360 (1945); (c) Johnson and Petersen, *ibid.*, **67**, 1366 (1945).

(3) (a) Ruzicka and Seidel, *Helv. Chim. Acta*, **5**, 369 (1922); (b) Barnett and Cook, *J. Chem. Soc.*, 22 (1933); (c) Bardhan and Banerji, *ibid.*, 476 (1935); (d) N. N. Chatterjee, *J. Ind. Chem. Soc.*, **13**, 588 (1936); (e) Dutta, *ibid.*, **18**, 233 (1941).