

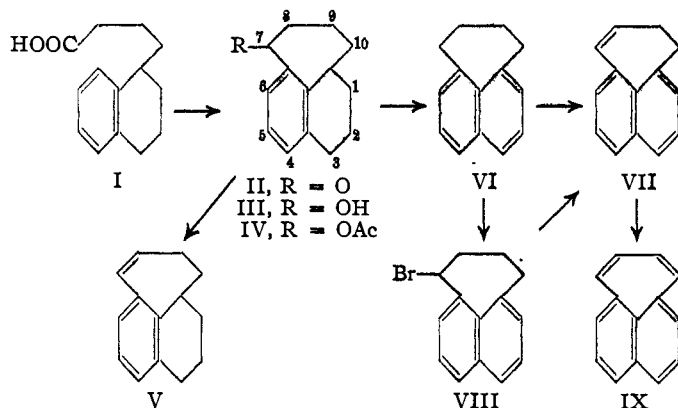
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Seven-membered Ring Compounds. II. 7,8-Dihydrocyclohepta[de]naphthalene, 1,2,8,9,10,10a-Hexahydrocyclohepta[klm]benz[e]indene and the Attempted Synthesis of Cyclohepta[de]naphthalene¹

BY PETE D. GARDNER² AND W. J. HORTON

Several methods have been investigated in an attempt to introduce a functional group into the aliphatic portion of 7,8,9,10-tetrahydrocyclohepta[de]naphthalene (VI). Further transformations have led to the synthesis of VII but the fully conjugated parent IX could not be obtained. Two alternate series of reactions on XIII gave an identical hydrocarbon XVI containing a hydroazulene ring fused to naphthalene.

The cyclization of tetrylbutyric acid (I) to the ketone II in high yield³ has made further study of such compounds possible. A structure of particular interest is the fully conjugated hydrocarbon IX.⁴



In an attempt to dehydrogenate 7-keto-1,2,3,7,8,9,10,10a-octahydrocyclohepta[de]naphthalene (II) with palladium-charcoal, hydrogen was eliminated with the simultaneous loss of the keto group and the only product isolated was the hydrocarbon VI. The carbinol III obtained by reduction of the ketone II also gave the hydrocarbon VI when heated with palladium-charcoal. The temperature required for dehydrogenation undoubtedly caused dehydration of the carbinol to the olefin V and the addition of hydrogen to the olefin is in accord with known cases.⁵ Dehydrogenation of the carbinol is a better method for the preparation of VI than the two step procedure originally used.³ The carbinol was converted to the carbinol acetate IV in the hope that dehydrogenation alone might take place. At a surprisingly low temperature (160°) the material lost acetic acid and dehydrogenation of the material gave VI as before.

The most satisfactory method for the preparation of VII from VI which repeatedly gave the same compound used bromine in cold carbon tetrachloride with illumination by tungsten lamps followed by dehydrohalogenation. The product

VII absorbed one mole of hydrogen over platinum to give VI indicating that no rearrangement of the carbon skeleton had taken place.

N-Bromosuccinimide (NBS) in the presence of peroxide⁶ or lead tetraacetate attacked the aliphatic ring of VI⁷ to give VIII but neither reaction could be repeated.

Attempts to obtain the diolefin IX from VI or from VII gave only unstable material.

The reaction of methyl bromoacetate and zinc with II proceeded in the usual manner and a soluble Reformatsky complex was obtained. On decomposition of the complex an oil X was obtained which could not be crystallized. It was characterized by conversion to the crystalline carbinol acid. The Reformatsky ester was dehydrated by means of formic acid and saponified to give a solid unsaturated acid XII. The unsaturated acid was reduced by hydrogen over platinum.

Two procedures were employed to convert the saturated acid XIII to the final product. In the first method the acid was cyclized with phosphorus pentoxide dissolved in orthophosphoric acid in quantitative yield using a slight modification of the published procedure.³ The same cyclization product XIV was obtained in high yield when the acid chloride was treated with stannic chloride for 60 seconds. It was found that the amount of ketone XIV produced by this method varied with the manner in which the acid chloride was prepared. If the acid XIII and phosphorus pentachloride in benzene were heated at once without standing at room temperature for 4 hours, the yield of ketone XIV decreased to 21% and the original acid XIII was recovered.

The ketone XIV was reduced by the conventional method and the product XV was dehydrogenated over palladium-charcoal to give XVI.

The second procedure utilized dehydrogenation of the acid XIII in the form of its methyl ester followed by cyclization of the saponification product XVII to the ketone XVIII by the methods used above. Cyclization of the acid chloride with stannic chloride was not as convenient as phosphorus pentoxide-orthophosphoric acid.³ The latter gave a 94% yield of purified product when heated for only 7 minutes. The hydrocarbon XVI obtained when the keto group was reduced proved to be identical to the material obtained in the alternate way.

(1) Presented at the Cleveland Meeting of the American Chemical Society, April 9, 1951.

(2) In part from the Masters Dissertation of Pete D. Gardner, University of Utah, 1950.

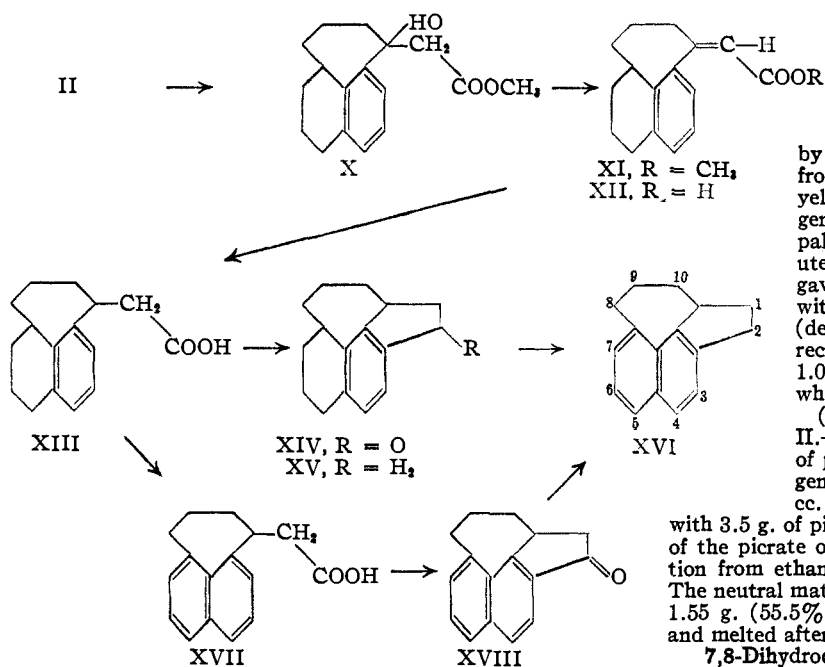
(3) R. C. Gilmore and W. J. Horton, *THIS JOURNAL*, **73**, 1411 (1951).

(4) The single example of such a structure has recently been reported by V. Boekelheide, W. E. Langeland and Chu-Tsin Liu, *ibid.*, **73**, 2432 (1951).

(5) W. E. Bachmann and A. L. Wilds, *ibid.*, **60**, 624 (1936).

(6) H. Schmidt and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

(7) The action of lead tetraacetate is in contrast to its attack on acenaphthene. J. Casas, *Opp. Syntheses*, **23**, 1 (1941).



The hydrocarbon XVI could not be converted to pyrene even though strongly heated under nitrogen with palladium-charcoal.

This work has been greatly assisted by a Frederick Gardner Cottrell Grant for which we express our great appreciation.

Experimental⁸

7,8,9,10-Tetrahydrocyclohepta[de]naphthalene (VI) (a) By Reduction to the Carbinol III and Dehydrogenation.—To 0.80 g. of lithium aluminum hydride suspended in 200 cc. of anhydrous ether was added slowly with mechanical stirring 8.0 g. of II in 200 cc. of ether. The reaction mixture was allowed to stand at room temperature for 15 minutes and the excess reducing agent was then destroyed by the cautious addition of water. The mixture was acidified with hydrochloric acid and the ether layer was separated and washed 4 times with water. A light yellow oil III remained after the ether was removed by distillation. The oil crystallized slowly over a 2-week period. A sample repeatedly crystallized from benzene-petroleum ether (30–60°) and from ethyl acetate-petroleum ether (30–60°) melted at 93–94°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97. Found: C, 83.38; H, 9.03.

The carbinol from 8.0 g. of ketone was combined with 200 mg. of palladium-charcoal⁹ and heated in an atmosphere of carbon dioxide at 275–280°. The hydrogen collected (1160 cc.) corresponded to the theoretical volume for 1 mole per mole of carbinol used. The product in ether was filtered to remove the catalyst and the residue after distillation of the ether was combined with 9.16 g. of picric acid and warmed with ethanol. On cooling, an orange picrate was obtained which melted at 101–102° after crystallization from ethanol and weighed 12.0 g. Repeated washing of an ether solution of this picrate with 2% aqueous ammonia and distillation of the dried ether solution gave after recrystallization from methanol 4.20 g. (60.5% from II) of crystals m.p. 55–56° unchanged on mixing with a known sample.⁹

(b) By Dehydrogenation of the Carbinol Acetate IV.—The carbinol III obtained as above from 3.0 g. of ketone was treated with 4 cc. of acetic anhydride and 2.4 cc. of pyridine in 100 cc. of anhydrous ether for 48 hours at room temperature. The solvent was distilled from a water-bath (80–85°) at 18 mm. The residue in ether was washed repeatedly with 5% hydrochloric acid and with water. After drying and distillation of the ether, a nearly colorless oil IV remained. The oil was combined with 0.10 g. of palladium-

charcoal⁹ and heated under nitrogen. At 160° refluxing acetic acid prevented further temperature rise and hydrogen evolution. The oil was therefore taken up in ether, filtered and the ether and acetic acid removed

by distillation. Distillation of the residue from a bath at 110° (0.10 mm.) gave a light yellow oil V. This material gave off hydrogen (230 cc.) in the presence of 50 mg. of palladium-charcoal at 290–300° for 30 minutes. Separation of the catalyst as before gave an oil which formed an orange picrate with 2.0 g. of picric acid, m.p. 103–105° (dec.). Decomposition of the picrate and recrystallization twice from methanol gave 1.0 g. (38%) of VI, m.p. 54–56°, unchanged when mixed with a known sample.⁹

(c) By Dehydrogenation of the Ketone II.—A mixture of 3.06 g. of II and 480 mg. of palladium-charcoal⁹ heated under nitrogen at 250–270° for 40 minutes gave off 300 cc. of hydrogen. The catalyst free product with 3.5 g. of picric acid in hot ethanol deposited 4.6 g. of the picrate of VI on cooling. Further recrystallization from ethanol gave picrate, m.p. 108–109° (dec.). The neutral material separated from the picrate weighed 1.55 g. (55.5%) after recrystallization from methanol and melted after 3 crystallizations at 55–56°.

7,8-Dihydrocyclohepta[de]naphthalene (VII).—A solution of 0.83 g. of VI in 25 cc. of dry carbon tetrachloride was treated at 0–5° with a solution of 0.74 g. of bromine in 18.5 cc. of carbon tetrachloride in a flask protected from moisture and exposed to a photographer's "Photo-flood" lamp. After 35 minutes the bromine color had faded. The solvent was distilled at 18 mm. at a temperature below 20° and the residue was treated with 2 cc. of triethylamine in 15 cc. of dry ether at room temperature for 15 minutes. After removal of the ether *in vacuo* an additional 3 cc. of the amine was added and the mixture was warmed to 60° for 2–3 minutes. The amine was removed as before and the residue in ether was washed with dilute hydrochloric acid and water. After drying and charcoal treatment the ether was distilled *in vacuo*. The residue with 1.8 g. of picric acid in methanol deposited 0.90 g. (48%) of bronze picrate, m.p. 125–128° (dec.) after 4 hours at 0°. The picrate for analysis was recrystallized from ethanol and melted at 131–133° (dec.).

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}_7\text{N}_3$: N, 10.27. Found: N, 10.1.

By decomposition of the picrate and recrystallization from methanol colorless plates were obtained which, after 5 crystallizations from methanol, melted at 43–45°. A mixture with VI melted at 45–56°. The pure material becomes oily on standing in air for 1–2 months and the analyses indicated small amounts of oxygen-containing material in spite of repeated purification.

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}$: C, 93.29; H, 6.71. Found: C, 92.56; H, 6.97.

Hydrogenation of 0.100 g. of VII in absolute alcohol over platinum at room temperature and pressure consumed 175 cc. of hydrogen (theory 160 cc.) and gave VI in quantitative yield, m.p. 54–56° after crystallization from methanol. The picrate of this material melted at 112–115°.

N-Bromosuccinimide followed by alcoholic potassium hydroxide converted VI to VII in 62% yield. Lead tetraacetate gave VII in 26% yield after separation from unreacted material by formation of the picrates. The reactions with these reagents however could not be repeated.

Attempted Preparation of Cyclohepta[de]naphthalene (IX) (a) From VI.—One gram (0.0055 mole) of VI in 17 cc. of carbon tetrachloride was refluxed with 2.94 g. of NBS (0.0165 mole) for 1.75 hours (free bromine noted). The cooled mixture was treated with 3 cc. of triethylamine and allowed to stand at room temperature for 10 minutes. Removal of the solids by filtration and the solvent by distillation *in vacuo* left a light tan oil which decomposed when picric acid and ethanol were added. The filtered carbon tetrachloride solution of the oil from another run was added to a column of Magnesol-Celite (5:1).¹⁰ Development of

(8) Melting points are uncorrected.

(9) N. D. Zelinsky and M. B. Turawa-Pollak, *Ber.*, **58**, 1205 (1925).

(10) J. M. Sugihara and M. L. Wolfrom, *THIS JOURNAL*, **71**, 3358 (1949). The material used was not washed and sieved as described in this paper.

the chromatogram with carbon tetrachloride appeared to be normal at first but after 10 minutes darkening was detected. Leaching of the cut column with acetone gave red viscous oils which darkened further and were finally abandoned.

(b) From VII.—In a manner similar to (a) VII was treated with NBS to produce a dark red oil unstable in air.

Methyl 7-Hydroxy-1,2,3,7,8,9,10,10a-octahydro-7-cyclohepta[de]naphthylacetate (X).—A solution of 12.0 g. of ketone II, b.p. 128–133° (0.3 mm.), in 600 cc. of 1:1 anhydrous ether and benzene was treated with 14.5 g. of zinc, 5.3 cc. of methyl bromoacetate and a crystal of iodine. After refluxing for 1 hour and adding a crystal of iodine and 5.3 cc. of methyl bromoacetate the mixture became cloudy and remained unchanged during the next 3 hours. A third 5.3-cc. portion of the bromoester was then added and the mixture was refluxed for a total of 7 hours. Very little insoluble complex precipitated. The mixture was treated in the usual way¹¹ and the light red oil obtained was distilled at 140–150° (1 mm.) to give 14.1 g. of light yellow oil which could not be crystallized.

Saponification of 3.4 g. of the distilled oil in aqueous potassium hydroxide gave on acidification an oil. This was collected in ether, dried and the ether distilled *in vacuo*. The residual oil in a small amount of hot ethyl acetate diluted with petroleum ether (30–60°) formed thick amber plates (1.13 g.) m.p. 129–130° (dec.) on cooling. After 5 crystallizations from the same solvent mixture it melted at 127–129° (dec.).

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 73.82; H, 7.74. Found: C, 74.24; H, 7.76.

1,2,3,7,8,9,10,10a-Octahydro-7-cyclohepta[de]naphthylacetic Acid (XIII).—A solution of 1.0 g. of the distilled Reformatsky ester X in 20 cc. of 90% formic acid was refluxed for 50 minutes. The cooled solution after dilution with water was extracted with ether and the dried ether solution was distilled. The residual oil (0.90 g.) was saponified with aqueous potassium hydroxide. Acidification gave a reddish-brown oil XII which crystallized in light pink rosettes (0.80 g., 85.5%), m.p. 98–103°, from petroleum ether (30–60°). After 4 crystallizations from light petroleum ether the m.p. was 101.5–103.5°. A few crystals readily decolorized a solution of bromine in carbon tetrachloride.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.74; H, 7.36.

Reduction of 0.80 g. of XII in acetic acid with platinum and hydrogen at a pressure slightly above atmospheric consumed 70 cc. of hydrogen (theory 70 cc.). After removal of the catalyst and solvent the residue crystallized. Recrystallization from aqueous methanol gave 0.80 g., m.p. 169–172°. After 4 crystallizations from anhydrous methanol it melted at 178–180°.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.45; H, 7.98.

In a run using 13.0 g. of X the over-all yield for dehydration, saponification and reduction was 76%.

2-Keto-1,2,5,6,7,7a,8,9,10,10a-decahydrocyclohepta[klm]benz[e]indene XIV (a) Using Stannic Chloride on the Acid Chloride.—A solution of 2.0 g. of the acid XIII in 40 cc. of anhydrous benzene was treated with 2.0 g. of phosphorus pentachloride and allowed to stand at room temperature for 4 hours. The solution became light green and then amber. It was refluxed on the steam-bath for 20 minutes and cooled to 5°. After addition of 4.78 g. of stannic chloride and vigorous shaking for 60 seconds the mixture was poured into concentrated hydrochloric acid and ice and diluted with an equal volume of water. The product was extracted with ether and the ether solution after washing with water was washed with 5% aqueous potassium hydroxide. Acidification of this alkaline layer gave no precipitate. The water washed and dried ether solution was distilled *in vacuo* and the residual oil crystallized in the ice chest overnight. Recrystallization from methanol gave 1.5 g. (81%) of XIV, m.p. 85–86°.

The acid chloride prepared by refluxing without an initial period at room temperature gave a 21% yield and the acid XIII was recovered in quantity.

(b) Using Phosphorus Pentoxide in Phosphoric Acid.—When 0.25 g. of XIII was cyclized according to the published

procedure⁸ the ketone XIV was obtained in 42.5% yield. The following modification gave better results. To a solution of 50 g. of phosphorus pentoxide in 32 g. of 85% orthophosphoric acid was added 2.1 g. of XIII and the mixture was heated to about 150° by swirling the flask above a free flame for one minute or until the solid particles had melted and the reaction mixture was homogeneous. A dark red color appeared after several minutes. After cooling to 100° the flask was heated on the steam-bath for 2 hours with frequent shaking and again warmed for 1 minute over a flame. The mixture was then cooled and treated as described.⁸ The recovered acid was negligible and the ketone solidified at once. Purification from methanol–water gave 1.9 g. (quantitative), m.p. 84–85° not changed on mixing with material from (a). Four crystallizations from aqueous methanol gave material, m.p. 86.5–87.5°.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.56; H, 7.87.

The semicarbazone in quantitative yield melted at 211–212° (dec.) when crystallized repeatedly from alcohol.

Anal. Calcd. for $C_{17}H_{21}ON_3$: N, 14.83. Found: N, 15.0.

1,2,3,9,10,10a-Hexahydrocyclohepta[klm]benz[e]indene (XVI).—The usual Clemmensen procedure¹² on 1.29 g. of XIV with a 30-hour reaction period gave 1.20 g. of light amber oil XV which gave a slight cloudiness with 2,4-dinitrophenylhydrazine. The Clemmensen product (0.60 g.) with 60 mg. of palladium-charcoal⁹ heated under nitrogen for 30 minutes at 280–290° gave 105 cc. of hydrogen (theoretical for 2 moles, 174 cc.). The oil free of catalyst was combined with 0.610 g. of picric acid to produce a red complex at once. The complex was dissolved in warm alcohol and allowed to stand at –20° for 24 hours. The solution deposited tiny red rhombs, m.p. 129°. From more dilute solutions a yellow amorphous solid separated. Concentration of the same solution gave red crystals when seeded and rubbed. The highly purified picrate displayed the same behavior. After several crystallizations from alcohol it melted at 128–129°.

Anal. Calcd. for $C_{22}H_{19}O_7N_3$: N, 9.61. Found: N, 9.55.

Treatment of the picrate with dilute ammonia gave colorless crystals which were recrystallized from aqueous isopropyl alcohol and from aqueous methanol to give 0.25 g. (42% from XIV), m.p. 63–65°. Further recrystallization from aqueous methanol gave branched needles or plates, m.p. 65–67°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.86; H, 7.70.

The semicarbazone of XIV with alcoholic sodium ethoxide at 180° (Wolf-Kishner) gave an oil which could not be crystallized. This oil with palladium-charcoal gave off no hydrogen and the resulting oil formed no picrate.

7,8,9,10-Tetrahydro-7-cyclohepta[de]naphthylacetic Acid (XVII).—The acid XIII (3.5 g.) was esterified with diazomethane from 5.0 g. of N-nitrosomethylurea.¹³ The ester was a light amber oil (4.0 g.). On heating 2.0 g. with 50 mg. of palladium-charcoal⁹ under nitrogen at 270–280° for 1.5 hours 450 cc. of hydrogen was collected (theoretical for 2 moles). The amber oil obtained could not be crystallized. It was saponified with potassium hydroxide in aqueous methanol. The acid XVII crystallized when moistened with petroleum ether (30–60°) and rubbed while cold. Crystallization from aqueous methanol and from benzene–petroleum ether (30–60°) gave 1.06 g. (68%), m.p. 127–128°. Four crystallizations from aqueous methanol gave material, m.p. 124–126°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.97; H, 6.71. Found: C, 79.54; H, 6.65.

2-Keto-1,2,8,9,10,10a-hexahydrocyclohepta[klm]benz[e]indene XVIII (a) Using Stannic Chloride.—Using the procedure above for the cyclization of XIII 0.86 g. of XVII with 1.04 g. of phosphorus pentachloride, 2.4 g. of stannic chloride and a reaction time of 15 minutes at room temperature gave no recovered acid and an amber oil which crystallized from methanol as amber needles, 0.50 g. (65%), m.p. 96–98°. When crystallized 4 times from methanol it melted at 97.5–99.5°.

(12) E. L. Martin, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 166.

(13) W. E. Bachmann and W. S. Struve, *ibid.*, p. 50.

(11) W. E. Bachmann, W. Cole and A. L. Wilds, *THIS JOURNAL*, **68**, 824 (1940).

Anal. Calcd. for $C_{18}H_{14}O$: C, 86.45; H, 6.34. Found: C, 86.25; H, 6.15.

(b) **Using Phosphorus Pentoxide in Phosphoric Acid.**—The acid XVII (0.570 g.) was added to a solution of 13 g. of phosphorus pentoxide dissolved in 9 cc. of 85% orthophosphoric acid³ and the mixture was heated on the water-bath for 7 minutes. Isolation as usual³ gave after crystallization from methanol-water 0.49 g. (94%) m.p. 93–99°. Mixed with the compound from (a) it melted at 95–99°.

The semicarbazone was obtained in quantitative yield and melted after extensive crystallization from ethanol at 225–226° (dec.).

Anal. Calcd. for $C_{17}H_{17}ON_3$: N, 15.04. Found: N, 14.7.

1,2,8,9,10,10a-Hexahydrocyclohepta[kim]benz[e]indene (XVI).—Clemmensen reduction¹² of 0.40 g. of XVIII with

a 30-hour reaction period gave an oil which formed a complex when 0.413 g. of picric acid was added. The picrate crystallized from alcohol when seeded with the picrate previously obtained and melted at 128–129°. The hydrocarbon from the picrate melted at 63–65° after 2 crystallizations from methanol-water and on mixing with XVI obtained above the m.p. was unchanged. The yield was 0.20 g. (54%). Attempts to reduce the ketone (Wolff-Kishner) failed as before.

Attempted Preparation of Pyrene from XVI.—Seventy mg. of XVI with 70 mg. of palladium-charcoal heated at 340–400° under nitrogen for 1 hour gave 70 cc. of hydrogen. The brown oil obtained could not be crystallized and addition of 90 mg. of picric acid gave a tar-like solid which resisted purification.

SALT LAKE CITY, UTAH

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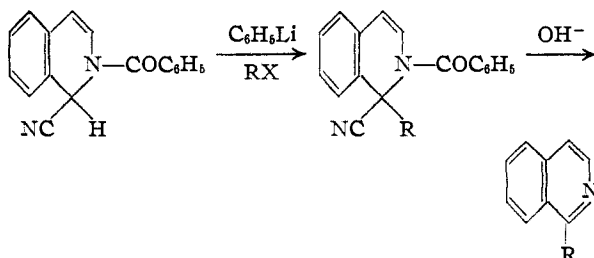
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Reissert Compounds. Further Alkylation Studies and a Novel Rearrangement¹

BY V. BOEKELHEIDE AND JOSEPH WEINSTOCK

In a previous study it was shown that 2-benzoyl-1-cyano-1,2-dihydroisoquinoline could be alkylated using certain Mannich bases. This work has now been extended to show that Reissert compounds of both the isoquinoline and quinoline series can be readily alkylated using alkyl halides. Since these alkylated Reissert compounds can be easily hydrolyzed with aqueous base to the corresponding substituted aromatic heterocycles, this represents a convenient method of preparing various substituted quinoline and isoquinoline derivatives. In the course of this study it was discovered that Reissert compounds, on heating in the presence of strong base, undergo a rearrangement to yield the corresponding aromatic C-acyl heterocycles.

In a previous communication it was reported that 2-benzoyl-1-cyano-1,2-dihydroisoquinoline could be alkylated by treatment with certain Mannich bases and that the resultant products could readily be hydrolyzed with aqueous base to the corresponding 1-substituted isoquinoline derivatives.² Since this procedure would be much more useful if alkyl halides could be used as well as Mannich bases in the alkylation step, we have extended our previous study and are now able to report that, under the proper conditions, Reissert compounds are smoothly alkylated by various alkyl halides. As shown in the equations below, 2-benzoyl-1-cyano-1,2-dihydroisoquinoline has been converted by this two-step procedure to 1-methyl-, 1-benzyl- and 1-*n*-butylisoquinoline, respectively, in yields ranging from 41 to 78%.



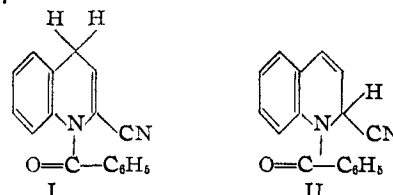
In order to obtain a good yield in the alkylation step, it was necessary that the conversion of the Reissert compound to its anion be done under mild conditions. Phenyllithium in an ether-dioxane solution proved to be the most satisfactory of the reagents investigated for this purpose, although

(1) Aided by a grant from the National Foundation for Infantile Paralysis, Inc.

(2) V. Boekelheide and C. Ainsworth, *THIS JOURNAL*, **72**, 2134 (1950).

ethylmagnesium bromide could also be employed. In the conversion to the isoquinoline derivatives the isolation of the intermediate alkylation product was found to be unnecessary and, in those instances where these intermediates were oils, their isolation was not attempted. The identity of the isoquinoline derivatives was established in each case either by direct comparison with an authentic specimen or by preparation of suitable derivatives. The overall procedure would appear to have many practical applications and to be superior to previous methods of preparing such derivatives as 1-methylisoquinoline.³

In the case of the Reissert compound derived from quinoline, methylation followed by alkaline hydrolysis gave lepidine in good yield. Although quinaldine might have been anticipated as a product, none was isolated from the reaction mixture. This result raised the question as to whether the intermediate alkylation product (III) should be assigned a 1,2-dihydro or a 1,4-dihydro structure. Actually, of course, it was not certain whether the quinoline Reissert compound possessed structure II, as commonly written, or whether it should be written as I.



Recently Seeley, Yates and Noller have examined the two isomeric quinoline 1,2-dicyanides and by a comparison of the ultraviolet spectra of the two iso-

(3) R. S. Barrows and H. J. Lindwall, *ibid.*, **64**, 2430 (1942); R. Schlttler and J. Müller, *Helv. Chim. Acta*, **31**, 914 (1948).