[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Dienone–Phenol Rearrangement. III. Rearrangement of 1-Keto-4,4-tetramethylene-1,4-dihydronaphthalene

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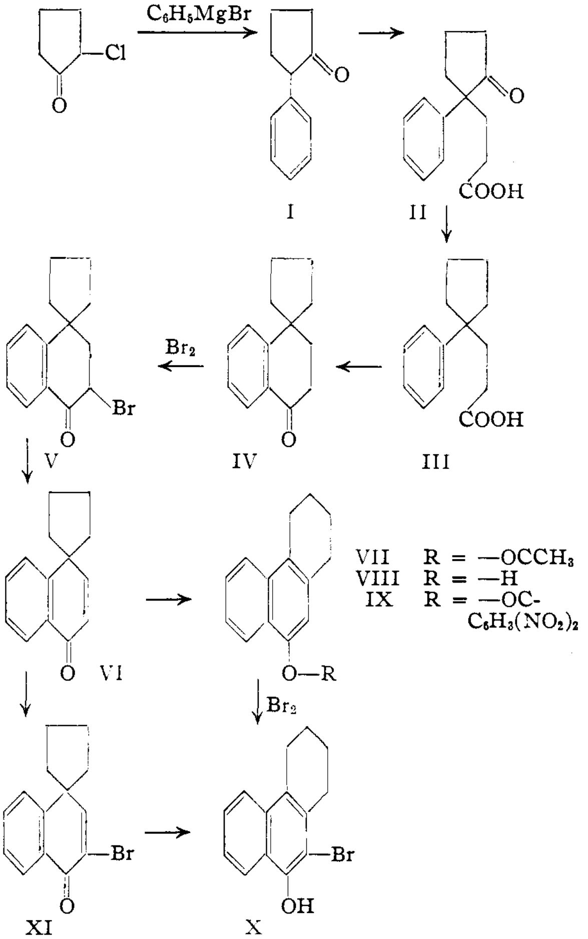
Since the dienone–phenol rearrangement of 1-keto-4,4-disubstituted-1,4-dihydronaphthalenes has produced such excellent yields of 3,4-disubstituted-1-naphthols,[2] the use of this rearrangement for the synthesis of tricyclic compounds seemed feasible. For this purpose the acid catalyzed rearrangement of the spirodienone VI to 1,2,3,4-tetrahydro-9-phenanthryl acetate (VII) was studied. This reaction represents a new method, free of inhibiting steric factors, for the preparation of rings containing six or more carbon atoms.

The synthesis of 1-keto-4,4-tetramethylene-1,4-dihydronaphthalene (VI) is shown in the accompanying diagram. 2-Phenylcyclopentanone (I) was prepared by the reaction of 2-chlorocyclopentanone with phenylmagnesium bromide. Since the melting point of our 2-phenylcyclopentanone did not agree with that previously reported,[3] the oxime, the semicarbazone and the tricyanoethylation product were prepared and analyzed to confirm its structure. This ketone, I, added readily to methyl acrylate to yield, after saponification, β-(1-phenyl-2-ketocyclopentyl)-propionic acid (II). Removal of the keto group was accomplished by a modified Wolff–Kishner reduction,[4] and the resulting acid, III, was cyclized to 4,4-tetramethylene-1-tetralone (IV). This ketone had been prepared previously by Levitz and Bogert[5] by the oxidation of 1,1-tetramethylenetetralin with chromic acid. Bromination and subsequent dehydrobromination of this ketone, IV, produced 1-keto-4,4-tetramethylene-1,4-dihydronaphthalene (VI).

By treatment with a solution of sulfuric acid in acetic anhydride, the spirodienone, VI, was rearranged in 95% yield to 1,2,3,4-tetrahydro-9-phenanthryl acetate (VII). Hydrolysis of this acetate gave the naphthol, VIII, which was brominated to 2-bromo-1,2,3,4-tetrahydro-9-phenanthrol (X). The ease of rearrangement of the spirodienones was demonstrated by an attempt to prepare the bromodienone, XI. Under the usual conditions for the preparation of these substances,[2] the spirodienone, VI, gave a mixture of the bromonaphthol, X, and a neutral oil which was probably XI, but which was not characterized.



To confirm the structure of the rearrangment product, 1,2,3,4-tetrahydro-9-phenanthrol (VIII) (m. p. 106–107°) was synthesized independently by the hydrolysis of 9-acetylamino-1,2,3,4-tetrahydrophenanthrene.[6] This sample and its acetate were identical with the products obtained from the dienone–phenol rearrangement. Cook, Hewett and Robinson[7] have described 1,2,3,4-tetrahydro-9-phenanthrol as a viscous liquid obtained in poor yield by the cyclization of 2-phenyl-Δ^1-cyclohexenylacetic acid. The product was characterized by means of its 3,5-dinitrobenzoate, m. p. 220°; the 3,5-dinitrobenzoate of our rearranged product melted at 221–222°. The product described by V. Braun and Bayer,[8] m. p. 114–115°, which they believed to be either 1,2,3,4-tetrahydro-9-phenanthrol, or 1,2,3,4-tetra-

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[1] Abstracted from a thesis presented to the Graduate Faculty of the University of Minnesota by Jay S. Buckley, Jr., in partial fulfilment of the requirements for the Ph.D. degree, October, 1949.

[2] R. T. Arnold, J. S. Buckley, Jr., and J. Richter, THIS JOURNAL, **69**, 2322 (1947); R. T. Arnold and J. S. Buckley, Jr., *ibid.*, **71**, 1781 (1949).

[3] Mitchovitch, *Compt. rend.*, **200**, 1601 (1935). Mitchovitch did not report an analysis for this material.

[4] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[5] Levitz and Bogert, *J. Org. Chem.*, **8**, 253 (1943).

[6] Bachman and Cronyn, *ibid.*, **8**, 456 (1943).

[7] Cook, Hewett and Robinson, *J. Chem. Soc.*, 168 (1939).

[8] V. Braun and Bayer, *Ber.*, **58**, 2667 (1925).

hydro-10-phenanthrol, or a mixture of these, obviously is not identical with VIII. This synthesis is now being used for the preparation of tricyclic compounds containing seven and eight membered rings.

Experimental

2-Phenylcyclopentanone (I).—To an ice-cold, stirred solution of phenylmagnesium bromide, prepared from 25.5 g. of magnesium and 164.7 g. of bromobenzene in 700 ml. of dry ether, was added a solution of 118.5 g. of 2-chlorocyclopentanone in 400 ml. of dry ether. The ether was removed by distillation and was replaced by 150 ml. of dry xylene. The black reaction mixture was finally heated at 150–170° (oil-bath temperature) for two hours. The cooled mixture was treated with ice and dilute hydrochloric acid, and the product was extracted with benzene. The organic layer was washed with water and dilute sodium hydroxide solution, then dried with sodium sulfate; the solvents were evaporated. Distillation of the residue yielded 80 g. (50%) of a light yellow oil, b. p. 135–140° (9 mm.). This material solidified when cooled. It was crystallized from 125 ml. of petroleum ether (b. p. 60–68°) to give 71 g. of 2-phenylcyclopentanone, m. p. 35–36°. A second crystallization of the compound from the same solvent raised its melting point to 36–37°. Mitchovitch[3] reported the compound to melt at 126–127°.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.27; H, 7.80.

2-Phenylcyclopentanone oxime, m. p. 139–140°, was purified by crystallization from aqueous alcohol. The compound is reported to melt at 146° (dec.).[3]

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.30; H, 7.48.

2-Phenylcyclopentanone semicarbazone, m. p. 213–214° (dec.), was purified by crystallization from alcohol. It is reported to melt at 228° (dec.).[3]

Anal. Calcd. for $C_{12}H_{15}N_3O$: C, 66.33; H, 6.96. Found: C, 66.35; H, 7.01.

2-Phenyl-2,5,5-tricyanoethylcyclopentanone.—A solution of 8 g. of 2-phenylcyclopentanone in 12 g. of acrylonitrile was added, during thirty minutes with stirring, to 75 ml. of *t*-butyl alcohol, which had been saturated previously with potassium hydroxide. The temperature was maintained at 25–30° during the addition and for an additional thirty minutes. The solution was then acidified with 50 ml. of dilute (1:4) hydrochloric acid and the resulting suspension stirred at 0° until the product solidified (two hours). By crystallization from methanol, 12 g. of the tricyanoethylation product, m. p. 72–77°, was obtained. Further crystallization of the product from methanol and from aqueous ethanol raised its melting point to 81.5–83°.

Anal. Calcd. for $C_{20}H_{21}N_3O$: C, 75.21; H, 6.63. Found: C, 75.05; H, 6.52.

β-(1-Phenyl-2-ketocyclopentyl)-propionic Acid (II).—A stirred solution of 32.0 g. of 2-phenylcyclopentanone in 125 ml. of dry benzene was treated with 0.1 g. of powdered sodium hydride. The mixture was heated to 40°, and a solution of 17.2 g. of methyl acrylate in 50 ml. of dry benzene was slowly added over a period of one hour. The exothermic reaction kept the temperature at 40–42°. The solution was stirred for one hour after the addition was completed, then was shaken with dilute hydrochloric acid, water, dilute sodium hydroxide, and finally with water. The benzene solution was dried with sodium sulfate, then evaporated. The viscous residue (48.5 g.) was hydrolyzed by boiling with 350 g. of 5% sodium hydroxide solution. The resulting solution was cooled, extracted once with ether, and the aqueous layer was acidified. The acid, thus obtained, was decolorized with carbon in hot alcohol. Water was added to the clarified alcoholic solution until it became cloudy. When cooled, the solution deposited 40.0 g. (86.3%) of a colorless, crystalline acid, m. p. 96.5–98°.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.51; H, 6.91.

The monobenzal derivative of the ketoacid (II) was readily obtained by the reaction of 1.16 g. of the acid (II) with 1.2 g. of benzaldehyde in a solution of 10 ml. of methyl alcohol and 10 ml. of 10% aqueous sodium hydroxide. Isolation of the acid in the usual way and crystallization from aqueous ethanol yielded 1.47 g. of colorless needles, m. p. 138–140°. After a second crystallization from the same solvent, the compound melted at 137.5–139°.

Anal. Calcd. for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29. Found: C, 78.51; H, 6.15.

β-(1-Phenylcyclopentyl)-propionic Acid (III).—A mixture of 40.0 g. of β-(1-phenyl-2-ketocyclopentyl)-propionic acid, 32.5 g. of potassium hydroxide, 24 ml. of 85% hydrazine, and 230 ml. of diethylene glycol was heated under reflux for two hours. Water was then removed by distillation until the internal temperature reached 195°. The resulting solution was heated under reflux at this temperature for four hours. The cooled solution was diluted with 300 ml. of water and acidified with 150 ml. of dilute (1:1) hydrochloric acid. Separation of the product by filtration, and crystallization from aqueous ethanol gave 30.6 g. (81.5%) of the desired acid (III), m. p. 75–76.5°. After crystallization from methanol, the analytical sample melted at 76–77°.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.05; H, 8.37.

4,4-Tetramethylene-1-tetralone (IV).—A stirred solution of 30 g. of β-(1-phenylcyclopentyl)-propionic acid in 150 ml. of dry benzene at 5–10° was treated with 32 g. of phosphorus pentachloride in small portions. After one hour at room temperature and five minutes at 70°, the solution was cooled to 0°, then treated with a solution of 35 ml. of stannic chloride in 35 ml. of benzene. The solution was stirred for fifteen minutes, then ice and hydrochloric acid were added to it. The complex hydrolyzed when the organic layer was shaken with 300 ml. of 10% sodium hydroxide solution. The benzene solution was dried with sodium sulfate and the benzene was removed by evaporation. Distillation of the residue yielded 24.6 g. (89.4%) of the desired tetralone, b. p. 131–132° (2 mm.); $n^{24}\text{D}$ 1.5732. Levitz and Bogert[5] reported the boiling point of this compound to be 140–142° (3 mm.); $n^{25}\text{D}$ 1.5716.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.90; H, 8.25.

The ketone formed a semicarbazone, m. p. 202–203°. The reported melting point[5] is 204.5–205.5°.

4,4-Tetramethylene-1-tetralone 2′,4′-dinitrophenylhydrazone crystallized from a mixture of ethyl acetate and alcohol and melted at 210.5–211.5°.

Anal. Calcd. for $C_{20}H_{20}N_4O_4$: C, 63.15; H, 5.30. Found: C, 63.03; H, 5.43.

2-Bromo-1-keto-4,4-tetramethylene-1,2,3,4-tetrahydronaphthalene (V).—Bromine (18.5 g.) was vaporized in a stream of dry nitrogen and absorbed, during forty-five minutes, in a solution of 23.1 g. of the tetralone, IV, in 250 ml. of carbon tetrachloride. After forty-five minutes at room temperature, the solution was washed with water and sodium bicarbonate solution. The residue from the evaporation of the dried carbon tetrachloride solution, after crystallization from aqueous methanol, yielded 27 g. of the bromoketone V, m. p. 51–53°. An additional 3.4 g. of bromoketone, m. p. 44–50°, were obtained from the methanolic mother liquors. Crystallization of this low melting fraction from petroleum ether (b. p. 60–68°) gave 2.1 g. of product, m. p. 51–53.5°. The total yield of relatively pure material was 90.3%. An analytical sample, m. p. 54–55°, was obtained by crystallization of the first fraction from petroleum ether (b. p. 60–68°).

Anal. Calcd. for $C_{14}H_{15}BrO$: C, 60.23; H, 5.41. Found: C, 60.11; H, 5.57.

1-Keto-4,4-tetramethylene-1,4-dihydronaphthalene (VI).—Dehydrobromination of 27.6 g. of the bromoketone, V, was accomplished by heating it under reflux for 70 minutes with 100 ml. of γ-collidine. The cooled mixture was treated with 300 ml. of ether and with 300 ml. of cold, dilute (1:2) hydrochloric acid. The ether solution was washed with water and sodium bicarbonate solution, and dried with sodium sulfate. Distillation gave 13.4 g. (68.5%) of the dienone, b. p. 147° (2 mm.); $n^{25}\mathrm{D}$ 1.5987.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.34; H, 7.35.

1,2,3,4-Tetrahydro-9-phenanthryl Acetate (VII).—A solution of 4.95 g. of the dienone, VI, in 50 ml. of acetic anhydride was treated with a solution of 0.50 g. of sulfuric acid in 25 ml. of acetic anhydride. After four hours at room temperature, the acetic anhydride was hydrolyzed with ice water. Filtration of the resulting suspension, gave 5.69 g. (95%) of 1,2,3,4-tetrahydro-9-phenanthryl acetate (VII), m. p. 78.5–81°. Crystallization from aqueous methanol gave 5.25 g. of the acetate, m. p. 80–81.5°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.68; H, 6.88.

1,2,3,4-Tetrahydro-9-phenanthrol (VIII).—Hydrolysis of 4.51 g. of the acetate, VII, by refluxing with 100 ml. of 5% methanolic potassium hydroxide for one hour gave (after acidification of the solution and crystallization of the compound from aqueous ethanol) 3.25 g. of 1,2,3,4-tetrahydro-9-phenanthrol (VIII), m. p. 104–106°. Crystallization of the compound from a mixture of carbon tetrachloride and petroleum ether (b. p. 60–68°) raised the melting point to 105.5–106.5°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.77; H, 7.16.

By crystallization from benzene, 1,2,3,4-tetrahydro-9-phenanthryl 3′,5′-dinitrobenzoate (IX), m. p. 221–222°, was obtained as lemon-yellow leaflets. This compound is reported[7] to melt at 220°.

1,2,3,4-Tetrahydro-9-phenanthrol (VIII) from 9-Acetylamino-1,2,3,4-tetrahydrophenanthrene.[9]—9-Acetylamino-1,2,3,4-tetrahydrophenanthrene[6] (1.50 g.) and 20 ml. of 15% sulfuric acid were placed in a Carius tube. Air was displaced with carbon dioxide, and the sealed tube was shaken thoroughly. The tube was heated at 240–260° for 3.5 hours; the contents of the tube were extracted with ether; the ether layer was dried with sodium sulfate, and the solvent evaporated. Distillation of the residue at a bath temperature of 200–220° (2 mm.) yielded 1.03 g. of an oil which solidified rapidly. Crystallization of the distillate from a mixture of carbon tetrachloride and petroleum ether (b. p. 60–68°) gave 0.85 g. of colorless crystals, m. p. 105–106.5°. A mixture of this compound with the tetrahydrophenanthrol from the preceding experiment showed no depression of melting point.

1,2,3,4-Tetrahydro-9-phenanthryl acetate, m. p. 80–81.5°, was prepared from the above tetrahydrophenanthrol with acetic anhydride. It did not depress the melting point of the acetate, VII, obtained by the dienone–phenol rearrangement.

2-Bromo-1,2,3,4-tetrahydro-9-phenanthrol (X).—(a) A solution of 594 mg. of the tetrahydrophenanthrol, VIII, in 10 ml. of acetic acid was treated with a solution of 480 mg. of bromine in five ml. of acetic acid. The resulting solution was poured into 75 ml. of water containing a trace of sodium bisulfite; the product solidified slowly. Crystallization from aqueous ethanol yielded 631 mg. of tan needles, m. p. 99–100°.

(b) An identical bromotetrahydrophenanthrol was obtained from an attempted preparation of the bromodienone, XI.

A solution of 3.96 g. of 1-keto-4,4-tetramethylene-1,4-dihydronaphthalene (VI) in 50 ml. of carbon tetrachloride was treated with a solution of 3.2 g. of bromine in 30 ml. of carbon tetrachloride. When the solvent was evaporated on the steam-bath, hydrogen bromide was evolved, but attempts to crystallize the residue failed. The residue was then treated with 150 ml. of ether and 150 ml. of water. Extraction of the ether layer with 80 ml. of 3% sodium hydroxide solution, followed by acidification of the alkaline solution, gave an oil that solidified rapidly. Crystallization from aqueous ethanol yielded 1.18 g. of 2-bromo-1,2,3,4-tetrahydro-9-phenanthrol, m. p. 99–100.5°.

Anal. Calcd. for $C_{14}H_{13}BrO$: C, 60.67; H, 4.73. Found: C, 60.60; H, 4.90.

Evaporation of the ether solution gave an oil, which was probably the bromodienone, XI. Attempts at crystallizing this oil failed.

Summary

1. 1-Keto-4,4-tetramethylene-1,4-dihydronaphthalene has been rearranged with sulfuric acid in acetic anhydride to 1,2,3,4-tetrahydro-9-phenanthryl acetate.

2. The rearrangement of spirodienones represents a new method, free of inhibiting steric factors, for the preparation of rings containing six or more carbon atoms.

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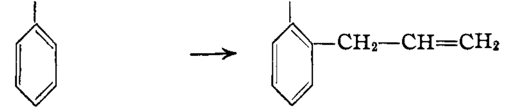
[9] We are indebted to Dr. John Richter for this experiment.

[CONTRIBUTION FROM CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN]

The Kinetics of the Rearrangement of Vinyl Allyl Ether[1]

BY FREDERIC W. SCHULER[2] AND GEORGE W. MURPHY

The rearrangement of aryl allyl ethers to yield allyl phenols, as illustrated by the rearrangement of phenyl allyl ether



Phenyl allyl ether *o*-Allylphenol

is known as the Claisen rearrangement.[3] The essential skeleton involved in the rearrangement has been demonstrated to be

$$C{=}C{-}O{-}C{-}C{=}C$$

for Hurd and Pollack[4] have synthesized the simplest compound with this skeleton structure, vinyl allyl ether, and have shown that it rearranges in the gas phase to give allylacetaldehyde.

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[1] An abstract of a thesis presented by Frederic W. Schuler to the faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, October, 1949.

[2] National Research Corporation, Cambridge, Massachusetts.

[3] See, for example, Tarbell in "Organic Reactions," Vol. II, Ch. 1, John Wiley and Sons, Inc., New York, N. Y., 1942.

[4] Hurd and Pollack, THIS JOURNAL, **60**, 1905 (1938).