[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KRISHNAGAR COLLEGE]

Spirocompounds. II. Synthesis of 1,2,3,4-Tetrahydronaphthalene-2,2-spiro-(2′-*n*-butylcyclopentane) and its Rearrangement on Catalytic Dehydrogenation

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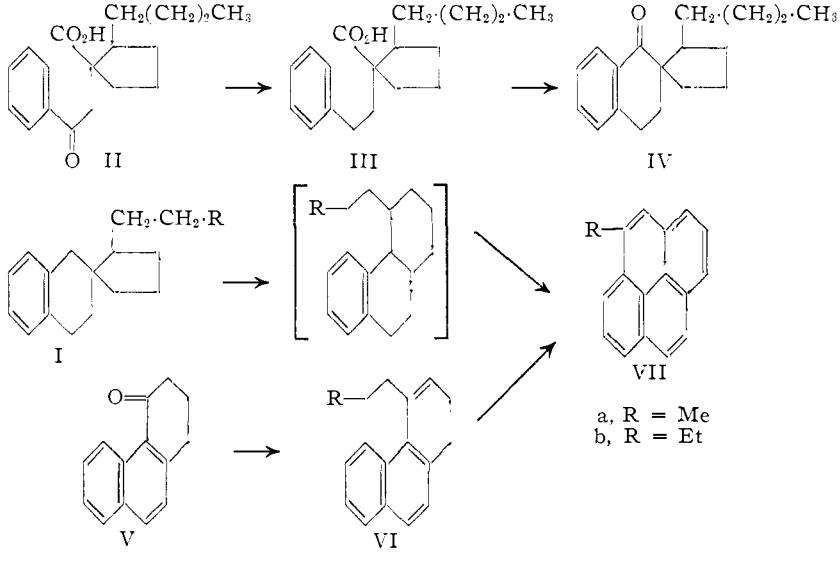
The spiran 1,2,3,4-tetrahydronaphthalene-2,2-spiro-(2′-*n*-butylcyclopentane) (Ib) has been synthesized. On dehydrogenation with platinum-on-charcoal catalyst at 300–350°, this spiran underwent a peculiar rearrangement and yielded 1-ethylpyrene (VIIb) as the sole product. A probable interpretation of this unusual ring transformation has been given. It has been found that 4-*n*-propyl-1,2-dihydrophenanthrene (VIa) and 4-*n*-butyl-1,2-dihydrophenanthrene (VIb) on dehydrogenation with platinum-on-charcoal under similar conditions yield 1-methylpyrene and 1-ethylpyrene, respectively.

In the first part[1] of this series, the platinum-catalyzed dehydrogenation of the spiran 1,2,3,4-tetrahydronaphthalene-2,2-spiro-(2′-*n*-propylcyclopentane) (Ia) to 1-methylpyrene was described. The peculiar rearrangement of this spiran on catalytic dehydrogenation was interpreted as occurring through the intermediate formation of a partially reduced 4-*n*-propylphenanthrene and cyclodehydrogenation of the latter to a pyrene derivative. In a series of papers[2,3] dealing with studies in catalytic dehydrogenation of alkyl substituted spirans, Sengupta and Chatterjee have noted that tetralin derivatives containing alkyl substituents in the α-position of the spirocyclopentane ring undergo ring transformation on dehydrogenation with platinum-on-charcoal to yield a phenanthrene derivative or a pyrene depending upon the nature of the alkyl group and in no case is the alkyl group eliminated. This rearrangement seems to be a general one and it seemed of interest to study the catalytic dehydrogenation of a spiran with a still heavier substituent in the spirocyclopentane ring. With this end in view, the spiran 1,2,3,4-tetrahydronaphthalene-2,2-spiro-(2′-*n*-butylcyclopentane) (Ib) was synthesized by an extension of the method developed earlier.[1] The anhydride of 2-*n*-butylcyclopentane-1-carboxy-1-acetic acid condensed with benzene in the presence of anhydrous aluminum chloride giving a single keto acid which was proved to be α,α-(2′-*n*-butylcyclopentane)-β-benzoylpropionic acid (II). The presence of the ketomethylene grouping in the keto acid was shown as in the previous cases by its reaction with salicylaldehyde in alcoholic solution in the presence of dry hydrogen chloride when a crimson-red pyrylium salt was obtained. The keto acid II was reduced by the Clemmensen method to α,α-(2′-*n*-butylcyclopentane)-γ-phenylbutyric acid (III) which on cyclization by 85% sulfuric acid afforded 1-keto-1,2,3,4-tetrahydronaphthalene-2,2-spiro-(2′-*n*-butylcyclopentane) (IV). This spiroketone did not condense with ethyl oxalate in presence of potassium ethoxide showing the absence of a ketomethylene grouping—an observation which may be considered as an additional evidence regarding correctness of the structure assigned to the keto acid II. On reduction by the Clemmensen method, the spiroketone yielded the desired spiran Ib. This spiran on dehydrogenation with platinum-on-charcoal underwent the same type of ring transformation as the propyl-substituted spiran (Ia),[1] yielding 1-ethylpyrene (VIIb) as the sole product of dehydrogenation. This ring transformation can be explained on the assumption, as in previous cases, that the spirocyclopentane ring undergoes fission near the heavy butyl group and the side chain so produced cyclizes in an angular manner forming a partially reduced 4-*n*-butylphenanthrene as an intermediate. This then undergoes cyclodehydrogenation, under the conditions of the experiment, with preferential formation of an additional six-membered ring, thus leading to ultimate production of 1-ethylpyrene.



This view of the possible formation of a 4-*n*-butylphenanthrene as an intermediate during dehydrogenation of the spiran Ib has been substantiated by the observation that 4-*n*-butyl-1,2-dihydrophenanthrene (VIb), prepared by the action of *n*-butylmagnesium iodide on 4-keto-1,2,3,4-tetrahydrophenanthrene (V) followed by dehydration, yielded 1-ethylpyrene (VIIb) on dehydrogenation

(1) D. N. Chatterjee, THIS JOURNAL, **77**, 414 (1955).

(2) S. C. Sengupta and D. N. Chatterjee, *J. Indian Chem. Soc.*, **29**, 438 (1952); **30**, 27 (1953); **31**, 11 (1954).

(3) S. C. Sengupta and D. N. Chatterjee, *ibid.*, **31**, 285, 911 (1954); **32**, 13 (1955).

with platinum-on-charcoal under identical conditions. Similarly, 4-*n*-propyl-1,2-dihydrophenanthrene (VIa) prepared from *n*-propylmagnesium iodide and the keto phenanthrene (V) afforded 1-methylpyrene (VIIa) on catalyzed dehydrogenation indicating, thereby, the intermediate formation of a 4-*n*-propylphenanthrene during dehydrogenation of the spiran (Ia).[1,4]

These observations, however, do not exclude the alternative possibility of the formation of a pyrene derivative from the spiran I as occurring through the following stages: (a) fission of the spirocyclopentane ring near the heavy alkyl group with the formation of a seven-carbon side chain (in the case of Ia) or an eight-carbon side chain (in the case of Ib) attached to the β-position of the naphthalene ring; (b) simultaneous double ring closure of the side chain by cyclodehydrogenation to a pyrene derivative.

Experimental[5]

2-*n*-Butylcyclopentanone.—The potassium derivative, prepared from 55 g. of 2-carbethoxycyclopentanone and 15 g. of powdered potassium in 300 ml. of xylene suspension was heated in an oil-bath at 120–130° for 12 hours after addition of 70 g. of *n*-butyl iodide. The product then was treated with cold water and the separated xylene layer was washed with water and dried. The solvent was removed under reduced pressure and the residual oil gave, on fractionation, 62 g. (82%) of 2-*n*-butyl-2-carbethoxycyclopentanone as colorless liquid, b.p. 127–128° (9 mm.), $n^{30}D$ 1.4480.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.92; H, 9.43. Found: C, 68.05; H, 9.35.

The semicarbazone crystallized from aqueous alcohol as colorless prisms, m.p. 162–163°.

Anal. Calcd. for $C_{13}H_{23}O_3N_3$: C, 57.98; H, 8.55. Found: C, 57.95; H, 8.50.

The foregoing butylated keto ester (62 g.) was hydrolyzed by boiling under reflux with 300 ml. of concentrated hydrochloric acid for 36 hours. The product was worked up as described in the previous paper[1] for 2-*n*-propylcyclopentanone to give 32 g. (80%) of 2-*n*-butylcyclopentanone boiling at 196–198°, $n^{30}D$ 1.4418.

The semicarbazone crystallized from aqueous ethanol in needles, m.p. 190° dec.

Anal. Calcd. for $C_{10}H_{19}ON_3$: C, 60.91; H, 9.64. Found: C, 60.85; H, 9.72.

Ethyl 2-*n*-Butylcyclopentylidinecyanoacetate.—A mixture of 28 g. of ethyl cyanoacetate, 35 g. of 2-*n*-butylcyclopentanone, 5 g. of ammonium acetate, 12 ml. of glacial acetic acid and 55 ml. of benzene was heated in an oil-bath at 130–140° for 6 hours and then at 140–150° for 12 hours while the water formed was removed with a modified Dean and Stark separator.[6] The mixture was cooled, diluted with 500 ml. of ether, washed with water, dried with sodium sulfate and the solvent removed. The residual oil, on fractionation, gave 52 g. (90%) of the unsaturated nitrile boiling at 165–167° (10 mm.), $n^{31}D$ 1.4784.

Anal. Calcd. for $C_{14}H_{21}O_2N$: C, 71.48; H, 8.93. Found: C, 71.34; H, 8.78.

It slowly absorbed bromine in chloroform solution and gave 2-*n*-butylcyclopentanone on oxidation.

2-*n*-Butylcyclopentane-1-carboxy-1-acetic Acid.—A solution of 32 g. of potassium cyanide in 62 ml. of water was added slowly to a solution of 52 g. of the foregoing unsaturated nitrile dissolved in 260 ml. of 95% ethanol. There was slight evolution of heat and the clear solution was allowed to stand for a week when a small amount of the potassium salt separated. Ethanol then was distilled off from water-bath and the dark semi-solid mass was acidified cautiously with dilute sulfuric acid. The liberated oil was extracted with 300 ml. of ether, washed with water, dried over sodium sulfate and the crude dicyanoester left after removal of ether was dissolved in 150 ml. of concentrated sulfuric acid. After allowing to stand for 24 hours, the solution was diluted cautiously with 200 ml. of water and then boiled under reflux for 36 hours. It was cooled in ice and the separated acid dissolved in warm aqueous sodium carbonate. Treatment with Norite, acidification of the alkaline filtrate with hydrochloric acid followed by crystallization of the separated acid from benzene–hexane mixture afforded 32 g. (60% based on the butylated ketone) of the dicarboxylic acid as fine needles melting at 125–126° dec.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.17; H, 8.77. Found: C, 63.21; H, 8.72.

The anhydride of the above dicarboxylic acid, obtained by heating the acid with excess of acetic anhydride for 6 hours was a colorless liquid, b.p. 173–175° (14 mm.), $n^{29}D$ 1.4725.

Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.57; H, 8.57. Found: C, 68.35; H, 8.40.

α,α-(2′-*n*-Butylcyclopentane)-β-benzoylpropionic Acid (II).—This acid was prepared by the action of 13.5 g. (0.1 mole) of powdered anhydrous aluminum chloride on a solution of 10.5 g. of the anhydride of 2-*n*-butylcyclopentane-1-carboxy-1-acetic acid in 35 ml. of dry benzene, according to the procedure described in the previous paper[1] for the corresponding propyl substituted keto acid. The keto acid when crystallized from petroleum ether (b.p. 60–80°) and then from aqueous alcohol yielded 12 g. (83%) of colorless needles melting at 126–127°. No isomeric keto acid could be isolated from the mother liquor.

Anal. Calcd. for $C_{18}H_{24}O_3$: C, 75.01; H, 8.33. Found: C, 74.95; H, 8.32.

The 2,4-dinitrophenylhydrazone, prepared in alcoholic sulfuric acid solution, crystallized from 95% ethanol in bright yellow prisms, m.p. 181°.

Anal. Calcd. for $C_{24}H_{28}O_6N_4$: C, 61.55; H, 5.98. Found: C, 61.53; H, 6.02.

The methyl ester of the keto acid, prepared by the action of methyl alcohol–hydrogen chloride on the acid, was a colorless liquid, b.p. 187–188° (8 mm.), $n^{23}D$ 1.5205.

Anal.. Calcd. for $C_{19}H_{26}O_3$: C, 75.50; H, 8.61. Found: C, 75.45; H, 8.62.

The Pyrylium Salt of the Keto Acid II.—A mixture of the keto acid (0.1 g.) and salicylaldehyde (0.1 g.) in absolute ethanol (10 ml.) was saturated with dry hydrogen chloride at 0°. The solution which gradually became deep red was kept in the ice-chest for three days when a crimson-red precipitate of the pyrylium salt appeared. This was filtered, washed with alcohol and dried *in vacuo*. It slowly dissolved in alkaline solution and did not melt up to 290°.

α,α-(2′-*n*-Butylcyclopentane)-γ-phenylbutyric Acid (III).—A mixture of 10 g. of the foregoing propionic acid II, 10 ml. of toluene, 50 g. of amalgamated zinc, 50 ml. of concentrated hydrochloric acid and 20 ml. of water was heated gently under reflux for 36 hours, a total of 50 ml. of concentrated hydrochloric acid being added at intervals within that period. It then was diluted with water and extracted with ether. The solvent was removed and the residual oil was dissolved in warm aqueous sodium carbonate. The butyric acid, which separated as a sticky mass on acidification of the alkaline filtrate, distilled at 195–197° (6–7 mm.) as a viscous liquid which soon solidified. After crystallization from petroleum ether (b.p. 40–60°) it afforded 6 g. (60%) of colorless needles, m.p. 115–118°. A mixed m.p. with the keto acid II was depressed. An analytical sample crystallized from methyl alcohol as stout needles, m.p. 119–120°.

Anal. Calcd. for $C_{18}H_{26}O_2$: C, 78.83; H, 9.48. Found: C, 78.45; H, 9.52.

1-Keto-1,2,3,4-tetrahydronaphthalene-2,2-spiro-(2′-*n*-butylcyclopentane (IV).—A mixture of 5 g. of the butyric acid III, 15 ml. of concentrated sulfuric acid and 5 ml. of water was heated on the steam-bath with stirring for 1.5 hours. The dark brown reaction mixture was poured on crushed ice and the ketone extracted with ether. The ether solution was washed with aqueous ammonia, then with water, dried with sodium sulfate and the solvent removed.

(4) Reviews on Aromatic Cyclodehydrogenation dealing with the dehydrogenation of 4-alkylphenanthrene recently have been published by G. Genie [*Ind. Chim. Belg.*, **16**, 576 (1951), and **18**, 670 (1953)].

(5) Melting points and boiling points are not corrected. Some of the analyses recorded here were carried out by Drs. Weiler and Strauss of Oxford.

(6) A. C. Cope, C. M. Hofmann, C. Wyckoff and E. Hardenbergh, THIS JOURNAL, **63**, 3452 (1941).

The residual oil on distillation afforded 3.5 g. (77%) of the spiroketone IV as colorless oil, b.p. 175–177° (7 mm.), $n^{23}D$ 1.5600. The spiroketone did not form a 2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_{18}H_{24}O$: C, 84.37; H, 9.37. Found: C, 83.95; H, 9.42.

Attempted Condensation of the Spiroketone IV with Ethyl Oxalate.—To a suspension of potassium ethoxide (prepared from 0.4 g. of powdered potassium and 0.5 ml. of absolute ethanol) in 15 ml. of dry ether, 1.6 g. of ethyl oxalate was added. The light yellow solution was cooled in ice and 2.5 g. of the spiroketone IV was added slowly. No salt of the condensation product separated even after keeping it for 16 hours. It was decomposed by ice and the neutral matter was taken up in ether. Removal of the solvent followed by distillation yielded 2.2 g. of the unchanged spiroketone. No condensation product could be isolated from the alkaline liquor on acidification.

1,2,3,4-Tetrahydronaphthalene-2,2-spiro-(2′-*n*-butylcyclopentane) (Ib).—Three grams of the preceding spiroketone IV was boiled gently under reflux with 15 g. of amalgamated zinc, 15 ml. of concentrated hydrochloric acid and 5 ml. of water for 48 hours with addition of 10-ml. portions of concentrated hydrochloric acid at 12-hour intervals. It was diluted and extracted with three 50-ml. portions of ether. The combined extract, which exhibited intense greenish fluorescence, was washed with water, dried over sodium sulfate, the ether evaporated and the residue was fractionated *in vacuo* to give 2 g. of the spirohydrocarbon boiling at 155–165° (7 mm.). This on refractionation gave 1.5 g. (50%) of the pure hydrocarbon as colorless mobile liquid having a characteristic odor, b.p. 155–157° (7 mm.), $n^{22}D$ 1.5318.

Anal. Calcd. for $C_{18}H_{26}$: C, 89.25; H, 10.75. Found: C, 88.81; H, 10.62.

Dehydrogenation of the Spirohydrocarbon (Ib) **with Platinum-on-charcoal.**—A mixture of 1 g. of the spirohydrocarbon and 0.1 g. of 10% platinum-on-charcoal catalyst[7] was heated in a metal-bath in an atmosphere of carbon dioxide at 300–330° for 4 hours and then at 330–350° for 2 hours more when evolution of hydrogen ceased. The liquid dehydrogenation product was extracted thoroughly with 100 ml. of ether. The extract which showed intense bluish-violet fluorescence, was filtered from catalyst, the solvent evaporated and the residual oil on distillation under reduced pressure yielded 0.5 g. of a liquid distillate. A portion of this (0.4 g.) was converted into picrate by warming with an equal amount of picric acid in ethanolic solution and the separated **picrate** (0.25 g.) after crystallization from absolute ethanol was obtained as long red needles, m.p. 184–185° (reported[8] 184.6–185.8°).

Anal. Calcd. for $C_{24}H_{17}N_3O_7$: C, 62.75; H, 3.70. Found: C, 62.74; H, 3.82.

The hydrocarbon was regenerated from the picrate by distribution between ammonia and ether. The ether solution was washed thoroughly with water and the residual oil (0.1 g.), left after removal of ether, slowly solidified. It crystallized from methyl alcohol in colorless plates having a bluish-violet fluorescence, m.p. 74–75° (reported[8] 74.8–75.3°). It dissolved in concentrated sulfuric acid giving an intense olive-green coloration.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.93; H, 6.07. Found: C, 93.72; H, 6.15.

The *sym*-trinitrobenzene complex was prepared with 0.1 g. of the original distillate. After three crystallizations from absolute ethanol, it was obtained as stout orange needles melting at 213–214° (reported[8] 209.4–210.2°).

Anal. Calcd. for $C_{24}H_{17}N_3O_6$: C, 65.01; H, 3.83. Found: C, 65.20; H, 3.89.

4-*n*-Propyl-1,2-dihydrophenanthrene (VIa).—A solution of 3 g. of 4-keto-1,2,3,4-tetrahydrophenanthrene (V) prepared by the method of Haworth[9] in 20 ml. of dry ether was added slowly from a dropping funnel with constant shaking to an ice-cooled solution of a Grignard reagent prepared from 0.4 g. of magnesium and 3 g. of *n*-propyl iodide in 10 ml. of dry ether. The yellow suspension was refluxed gently for four hours, and the complex was decomposed by ice and dilute sulfuric acid. The organic layer was separated, washed successively with 5% sodium thiosulfate solution, water and ether distilled off. The residual oil was dissolved in 50 ml. of 95% ethanol and heated with 1 g. of semicarbazide acetate on the water-bath for 1 hour when a little semicarbazone of the unreacted ketone V separated. It was filtered and the filtrate after concentration was diluted with water and extracted with ether. Removal of the solvent from the washed and dried extract gave an oil which was dehydrated by heating with 15 ml. of 98% formic acid for 1 hour. Dilution with water followed by extraction with ether afforded 2.2 g. (70%) of the hydrocarbon VIa as a colorless liquid boiling at 177–180° (8 mm.).

Anal. Calcd. for $C_{17}H_{18}$: C, 91.89; H, 8.11. Found: C, 91.56; H, 7.91.

The hydrocarbon formed a **picrate** in methyl alcoholic solution from which it separated in scarlet needles, m.p. 99–100°

Anal. Calcd. for $C_{23}H_{21}O_7N_3$: C, 61.20; H, 4.65. Found: C, 61.12; H, 4.48.

Dehydrogenation of 4-*n*-Propyl-1,2-dihydrophenanthrene (VIa). Formation of 1-Methylpyrene (VIIa).—One gram of the phenanthrene derivative VIa was heated with 0.1 g. of 10% platinum-on-charcoal catalyst in a metal-bath at 300–320° for 2 hours and then at 320–330° for 2 hours. Extraction of the melt with benzene, filtration, concentration and distillation under reduced pressure afforded 0.5 g. of a semi-solid distillate which was converted to the picrate by warming with 0.5 g. of picric acid in benzene solution. The separated **picrate** (0.7 g.) after one crystallization from absolute ethanol was obtained as long red needles melting at 227°. The hydrocarbon regenerated from the picrate crystallized from methyl alcohol as colorless flakes, m.p. 146–147°.

Anal. Calcd. for $C_{17}H_{12}$: C, 94.44; H, 5.56. Found: C, 94.32; H, 5.52.

When this sample was mixed with an equal portion of the pyrene derivative (m.p. 147°) which had been obtained by the dehydrogenation of the propyl substituted spiran Ia,[1] the melting point was 146–147°. **The *sym*-trinitrobenzene complex** crystallized from ethanol as orange needles, m.p. 250°. When mixed with this derivative of the dehydrogenation product of the spiran Ia[1] (m.p. 246–247°) the melting point was 246–249°.

4-*n*-Butyl-1,2-dihydrophenanthrene (VIb).—The reaction between the Grignard reagent (prepared from 0.4 g. of magnesium and 3.2 g. of *n*-butyl iodide in 10 ml. of ether) and 3 g. of the ketophenanthrene V was performed as described above for VIa. Separation of the unreacted ketone followed by dehydration and distillation afforded 1.6 g. (45%) of the phenanthrene derivative VIb as a colorless liquid, b.p. 180–182° (8 mm.).

Anal. Calcd. for $C_{18}H_{20}$: C, 91.53; H, 8.47. Found: C, 91.25; H, 8.32.

The hydrocarbon yielded a **picrate** in methyl alcoholic solution, which crystallized from methyl alcohol as scarlet needles, m.p. 115–116°.

Anal. Calcd. for $C_{24}H_{23}O_7N_3$: C, 61.93; H, 4.94. Found: C, 61.75; H, 4.85.

Dehydrogenation of 4-*n*-Butyl-1,2-dihydrophenanthrene (VIb). Formation of 1-Ethylpyrene (VIIb).—One gram of the foregoing phenanthrene derivative VIb was dehydrogenated by heating with 0.1 g. of 10% platinum-on-charcoal in a metal-bath at 300–330° for 2 hours and then at 330–350° for 2 hours more. Extraction with benzene followed by distillation under reduced pressure yielded 0.4 g. of a semi-solid distillate which was converted to the picrate in benzene solution. The separated **picrate** (0.4 g.) after one crystallization from absolute ethanol was obtained as long red needles, m.p. 183–184°, which was unchanged when mixed with this derivative of the dehydrogenation product of the spiran Ib.

The **hydrocarbon** regenerated from the picrate by the chromatographic method using activated alumina, crystallized from methyl alcohol as colorless plates, m.p. 74°. When this sample was mixed with the hydrocarbon obtained by the dehydrogenation of the spiran Ib it melted at 74–75°.

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(7) R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1127 (1940).
(8) M. S. Newman, *J. Org. Chem.*, **16**, 861 (1951).
(9) R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).