[CONTRIBUTION FROM THE ROLLIN H. STEVENS MEMORIAL LABORATORY OF THE DETROIT INSTITUTE OF CANCER RESEARCH]

A Synthesis of *trans*-10-Methyl-2-decalone[1]

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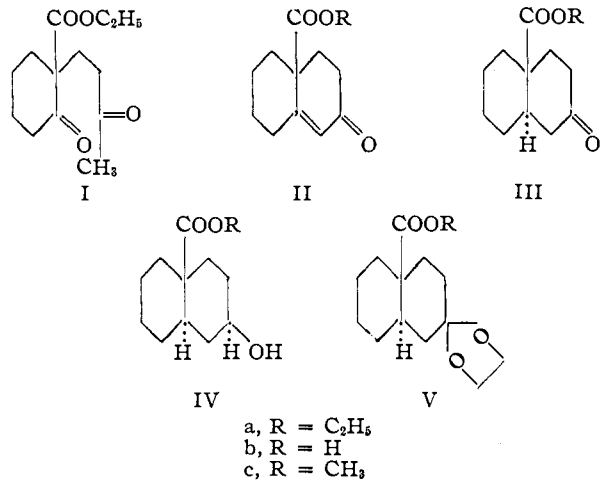
A convenient synthesis of *trans*-10-methyl-2-decalone is described.

The simplest available route to 10-methyl-2-decalone is the catalytic hydrogenation of 2-keto-10-methyl-$\Delta^{1:9}$-octahydronaphthalene.[2] The major product, however, is the *cis* isomer and the small amount of the *trans* isomer, formed along with it, has been obtained only by a mechanical separation of the crystals of the 2,4-dinitrophenylhydrazones.[3] A mixture of the *cis* and *trans* isomers of 3-carboxy-10-methyl-2-decalone separable by fractional crystallization, was obtained by the reduction of 2-keto-3-carboxy-10-methyl-$\Delta^{1:9,3:4}$-hexahydronaphthalene and of 2-keto-3-carboxy-10-methyl-$\Delta^{1:9}$-octahydronaphthalene. The *trans* isomer was then decarboxylated to *trans*-10-methyl-2-decalone (X).[4] The above methods are unsatisfactory for the preparation of large quantities of X because the desired isomer represents only the minor component in a mixture. The first practical synthesis of 10-methyl-2-decalone which could be directed to give predominantly the *trans* isomer X was developed by Woodward and co-workers.[3]

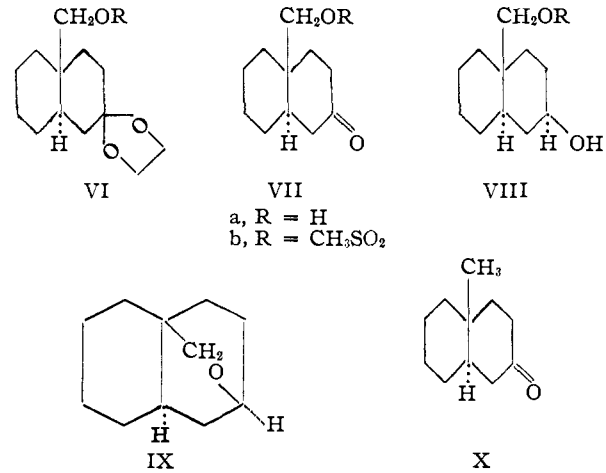
Recently, a novel approach was used for the synthesis of bicyclic compounds with angular methyl groups.[5] While it was originally thought that this method led to derivatives of *cis*-9-methyldecalin, it was subsequently shown that the products had the *trans* configuration at the ring juncture.[6] This opened up the possibility of a convenient stereospecific synthesis of *trans*-10-methyl-2-decalone (X), which will be described in this paper.

The condensation of 2-carbethoxycyclohexanone with methyl vinyl ketone in the presence of triton B permitted the isolation of 2-(3′-keto-1′-*n*-butyl)-2-carbethoxycyclohexanone (I), which was cyclized with sodium ethoxide to the unsaturated keto ester IIa.[2] Some saponification in the basic medium caused a small amount of 10-carboxy-$\Delta^{1:9}$-2-octalone (IIb) to be formed. The catalytic hydrogenation of IIa[5] produced predominantly *trans*-10-carbethoxy-2-decalone (IIIa), and the corresponding acid IIIb was reduced further with sodium borohydride to *cis*-10-carboxy-2-*trans*-decalol (IVb).[5]

The keto group in the saturated keto ester (IIIa or IIIc) was protected as the dioxolane (Va or Vc) and the ester group was reduced with lithium aluminum hydride in boiling ether to give *trans*-10-hydroxymethyl-2-decalone-2-dioxolane (VIa). Mild acid hydrolysis opened the dioxolane ring and afforded *trans*-10-hydroxymethyl-2-decalone (VIIa), characterized as the 2,4-dinitrophenylhydrazone. The hydroxydioxolane (VIa) was converted in good yield to the mesylate VIb which was hydrolyzed to the keto mesylate VIIb.



A sodium borohydride reduction converted the keto mesylate VIIb to a hydroxy mesylate, which probably has the free hydroxyl group in the more stable equatorial position[7] VIIIb, while lithium aluminum hydride reduced it to a mixture of *cis*-10-hydroxymethyl-2-*trans*-decalol (VIIIa)[5] and a camphoraceous oil which may have been the cyclic ether IX. It may be noted that sodium borohydride did not affect the mesylate portion of the molecule, while the reaction of lithium aluminum hydride with that group proceeded only slowly (allowing ether formation) and then almost exclusively at the sulfur atom.



(1) This work was supported by institutional grants to the Detroit Institute of Cancer Research from the American Cancer Society, Inc., the American Cancer Society, Southeastern Michigan Division, and The Kresge Foundation.

(2) E. C. duFeu, F. J. McQuillin and R. Robinson, *J. Chem. Soc.*, 53 (1937).

(3) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, THIS JOURNAL, **74**, 4223 (1952).

(4) A. S. Dreiding and A. J. Tomasewski, *J. Org. Chem.*, **19**, 241 (1954).

(5) A. S. Hussey, H. P. Liao and R. H. Baker, THIS JOURNAL, **75**, 4727 (1953). *Cf.* this paper for the nomenclature used in the present report.

(6) A. S. Dreiding and A. J. Tomasewski, *ibid.*, **77**, 168 (1955).

(7) D. H. R. Barton and N. J. Holness, *J. Chem. Soc.*, 78 (1952).

The removal of the oxygen on the angular carbon was accomplished in 82% yield by treating the dioxolane mesylate VIb with sodium hydrogen sulfide and treating the crude product with Raney nickel catalyst. The opening of the dioxolane ring by mild acid hydrolysis afforded pure *trans*-10-methyl-2-decalone (X). It is of interest that no isomerization at the ring juncture[8] took place during the prolonged treatment with the catalyst. This was shown by the direct replacement of the methanesulfonate radical in VIb with hydrogen, which was accomplished in 30% yield by a lithium (or sodium) and alcohol in liquid ammonia reduction, followed by acid hydrolysis.

The best synthetic scheme for the preparation of X is

$$\text{IIa} \xrightarrow{91\%} \text{IIIa} \xrightarrow{80\%} \text{Va} \xrightarrow{99\%} \text{VIa} \xrightarrow{79\%} \text{VIb} \xrightarrow{82\%} \text{X}$$

It is probably not necessary to isolate all the intermediates.

We are grateful to Dr. J. M. Vandenbelt and Mr. Bruce Scott of Parke, Davis and Co. for the ultraviolet and infrared absorption spectra.

Experimental[9]

2-(3′-Keto-1′-*n*-butyl)-2-carbethoxycyclohexanone (I).—To an ice-cold mixture of 85 g. (0.5 mole) of 2-carbethoxycyclohexanone[10] and 3 cc. of triton B was added dropwise 40 g. (0.57 mole) of methyl vinyl ketone over a period of 30 minutes with stirring and the mixture was allowed to stand at room temperature for 12 hours. The product was taken up in ether and washed consecutively with water, dilute hydrochloric acid, sodium bicarbonate and sodium chloride solution. After drying and concentrating, the residue was distilled and the diketo ester I was collected at 138–140° (0.4–0.5 mm.), $n^{25}D$ 1.4730, yield 110 g. (91%). The distillate did not give a positive ferric chloride test; it produced a yellow precipitate with 2,4-dinitrophenylhydrazine reagent in dilute sulfuric acid.

10-Carbethoxy-$\Delta^{1:9}$-2-octalone (IIa).—A solution of 80 g. (0.333 mole) of the diketo ester I and sodium ethoxide (made from 10 g., 0.435 mole, of sodium) in 500 cc. of anhydrous ethanol was allowed to stand at room temperature under an atmosphere of nitrogen for 2 hours. After acidification with glacial acetic acid and filtration of the sodium acetate formed, the filtrate was concentrated at reduced pressure and the residue taken up in benzene. The solution was washed with saturated sodium chloride and then with sodium bicarbonate solution. Acidification of the latter precipitated 10 g. (15% of **10-carboxy-$\Delta^{1:9}$-2-octalone (IIb)** as a yellow amorphous precipitate, m.p. 75–104°. Two recrystallizations from methylene chloride afforded slightly yellow thick needles, m.p. 130–131° dec., λ_{max}^{alc} 239.5 mμ (ε 12,360), yield 8.7 g. (13%).

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 68.04; H, 7.24.

The benzene solution of the ester was washed with saturated sodium chloride solution, dried over magnesium sulfate and concentrated. The residual unsaturated keto ester IIa was distilled at 125–132° (1 mm.), yield 51 g. (66%), $n^{25}D$ 1.5070. A small portion was converted to the **2,4-dinitrophenylhydrazone**, which crystallized from ethyl acetate–ethanol as crimson plates, m.p. 117–118°.

Anal. Calcd. for $C_{19}H_{22}N_4O_6$: C, 56.71; H, 5.51; N, 13.92. Found: C, 56.57; H, 5.54; N, 13.72.

trans-**10-Carboxy-2-decalone (IIIb).**—A solution of 50 g. of the unsaturated keto ester IIa, prepared as described in the preceding experiment, in 250 cc. of ethanol was shaken under 40 lb. of hydrogen in the presence of 1 g. of 10% palladium-on-charcoal catalyst for 30 minutes. These conditions apparently produced some over-hydrogenation as evidenced by the nature of the products. After filtration of the catalyst and evaporation of the alcohol, the residual oil was saponified in a hot solution of 20 g. of sodium hydroxide in 180 cc. of water and 10 cc. of alcohol for 8 hours. Acidification and ether extraction produced an oil which failed to crystallize. It was distilled at 140–170° (0.5–0.8 mm.) (large pot residue) to give a yellowish thick oil, which crystallized partially from ether and petroleum ether, yield 11.8 g. (27%), m.p. 82–85°. Recrystallization from the same solvents afforded an analytical sample of *trans*-**10-carboxy-2-decalone (IIIb)**, m.p. 91.5–93°, as dense clusters of prisms; $\lambda_{max}^{CHCl_3}$ 3.34(m), 5.83(s), 6.86(m), 7.08(w), 7.49(w), 7.67(m), 7.79(w), 8.03(m), 8.37(w), 8.51(w), 8.69(m), 8.82(w), 9.03(w), 9.63(w), 9.93(w), 10.14(w), 10.63(m) μ.

Anal. Calcd. for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.58; H, 8.51.

The material in the mother liquor from the crystallization of IIIb was treated with sodium bicarbonate solution and separated into a soluble and insoluble fraction. The soluble portion consisted of another crop of 4.5 g. (10%) of *trans*-10-carboxy-2-decalone (IIIb), m.p. 83–85°.

The insoluble fraction probably was the lactone of IVb; it was saponified with hot methanolic sodium hydroxide for two hours to give, after acidification, 2.56 g. (6%) of *cis*-10-carboxy-2-*trans*-decalol (IVb), m.p. 150–152°. Recrystallization from ether as long colorless prisms raised the m.p. to 160–161° (reported[5] 149.2–150.6°).

trans-**10-Carbethoxy-2-decalone-2-dioxolane (Va).**—Better results in the catalytic hydrogenation of the unsaturated keto ester IIa were obtained with Adams catalyst at atmospheric pressure. A solution of 26 g. of IIa in 150 cc. of ethanol was stirred under an atmosphere of hydrogen in the presence of 0.5 g. of Adams catalyst. The hydrogen uptake stopped after the consumption of one mole. Filtration, concentration and distillation of the residue gave *trans*-10-carbethoxy-2-decalone (IIIa) as a colorless oil, b.p. 115–135° (1 mm.), $n^{21.5}D$ 1.4820, yield 24 g. (91%) (reported[5] b.p. 146–148° at 2 mm., $n^{25}D$ 1.4790).

A solution of this distillate, 12 g. of ethylene glycol and 0.35 g. of *p*-toluenesulfonic acid monohydrate in 200 cc. of benzene was refluxed into a Dean–Stark trap for three hours, when all the water had separated. The solution was washed with saturated sodium bicarbonate and water, dried and concentrated. The residue was distilled at 115–122° (0.2 mm.) to give 23.1 g. (80%) of *trans*-**10-carbethoxy-2-decalone-2-dioxolane (Va)** as a colorless liquid, $n^{23}D$ 1.4850.

trans-**10-Carbomethoxy-2-decalone-2-dioxolane (Vc).**—A solution of 11.2 g. of *trans*-10-carboxy-2-decalone, m.p. 82–85°, in ether was treated with an excess of ethereal diazomethane. After extraction with a sodium bicarbonate solution, the ether was removed and the residue distilled at 110–113° (0.3 mm.) to give 10.7 g. (89%) of *trans*-10-carbomethoxy-2-decalone (IIIc), $n^{23}D$ 1.4895; $^*\lambda_{max}^{CHCl_3}$ 5.79(s), 5.84(s), 6.85(m), 6.95(m), 7.30(w), 7.50(m), 7.71(m), 7.81(w), 8.1(s), 8.34(s), 8.76(s), 9.00(m), 9.64(w), 10.03(m), 10.20(w), 10.72(w) μ.

This keto ester IIIc was converted to *trans*-**10-carbomethoxy-2-decalone-2-dioxolane (Vc)** by the procedure described in the preceding experiment, b.p. 119–130° (0.4–0.5 mm.), yield 12.8 g. (99%); $^*\lambda_{max}^{CHCl_3}$ 5.81(s), 6.86(s), 6.96(m), 7.31(m), 7.62(m), 7.71(w), 8.15(m), 8.39(s), 8.57(w), 8.64(w), 8.84(m), 9.06(s), 9.28(s), 9.61(w), 9.81(s), 10.00(w), 10.12(m), 10.60(w), 11.00(m) μ.

cis-**10-Carbomethoxy-2-*trans*-decalol (IVc).**—A solution of 185 mg. of *trans*-10-carboxy-2-decalone (IIIb), m.p. 91.5–93°, in 5 cc. of 2% aqueous sodium hydroxide was treated with 185 mg. of sodium borohydride, warmed for 5 minutes and allowed to stand at room temperature for 30 minutes. Acidification precipitated 130 mg. (69%) of *cis*-**10-carboxy-2-*trans*-decalol (IVb)**, m.p. 148–149°. Recrystallization from ether afforded large colorless prisms, m.p. 160–161° (reported,[5] 149.2–150.6°); $\lambda_{max}^{mineral\ oil}$ 2.89(m), 3.69(w), 3.77(w), 5.88(s), 6.56(w), 7.01(w), 7.59(m), 7.68(w), 8.00(w), 8.24(s). 8.40(m), 8.57(w), 8.68(w),

(8) W. E. Bachmann, A. Ross, A. S. Dreiding and P. A. S. Smith, *J. Org. Chem.*, **19**, 222 (1954).

(9) The melting points were measured on a Fisher–Johns block and are uncorrected. The analyses are by Micro-Tech Laboratories in Skokie, Ill. The infrared absorption spectra marked* were measured in a Baird double beam, and the others in a Beckman IR 2T instrument.

(10) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 531.

8.76(w), 8.89(w), 9.09(m), 9.59(s), 9.71(s), 10.05(w), 10.32(m), 10.47(w), 10.80(m), 11.04(w), 11.34(w), 11.64(w), 11.83(w), 12.44(s), 13.09(w), 13.85(s) μ.

Esterification of this acid with an excess of ethereal diazomethane formed the ***cis*-10-carbomethoxy-2-*trans*-decalol (IVc)**, which crystallized from ether–petroleum ether as colorless needles, m.p. 82–83°.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.28; H, 9.49.

***trans*-10-Hydroxymethyl-2-decalone-2-dioxolane (VIa).**—A solution of 21 g. (0.078 mole) of *trans*-10-carbethoxy-2-decalone-2-dioxolane (Va), b.p. 115–122° (0.2 mm.), and 5 g. (0.13 mole) of lithium aluminum hydride in 200 cc. of ether was refluxed for 12 hours. The excess reagent was decomposed with water, the ethereal layer was separated and concentrated, and the residue was distilled at 135–136° (0.2 mm.) to give 17.6 g. (99%) of ***trans*-10-hydroxymethyl-2-decalone-2-dioxolane (VIa)** as a very viscous oil; $^{*}\lambda_{max}^{CHCl_3}$ 2.92(m), 6.88(m), 7.36(m), 7.71(m), 8.2(s), 8.46(s), 9.10(s), 9.29(s), 9.75(s), 10.09(w), 10.31(m), 10.48(m), 10.60(m), 10.90(w) μ. A 0.2-g. portion, which was allowed to stand, crystallized and melted at 73–74° after recrystallization from ether–petroleum ether, yield 0.16 g. (80%).

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.13; H, 9.87.

Under identical conditions *trans*-10-carbomethoxy-2-decalone-2-dioxolane (Vc), b.p. 119–130° (0.4–0.5 mm.), was reduced to the same hydroxy–dioxolane (VIa) in 91% yield, b.p. 135–140° (0.2 mm.), $n^{25}D$ 1.5106.

When a solution of 250 mg. of this hydroxy–dioxolane in a little methanol was treated with 2,4-dinitrophenylhydrazine reagent in 50% aqueous sulfuric acid, and 87% yield of the **2,4-dinitrophenylhydrazone of *trans*-10-hydroxymethyl-2-decalone (VIIa)** crystallized slowly, m.p. 90–103°. Recrystallization from methyl acetate–methanol yielded an analytical sample as orange needles, m.p. 105–107°.

Anal. Calcd. for $C_{17}H_{22}N_4O_5$: C, 56.34; H, 6.12; N, 15.46. Found: C, 56.55; H, 6.42; N, 15.34.

Mesylate of *trans*-10-Hydroxymethyl-2-decalone-2-dioxolane (VIb).—To an ice-cold solution of 17 g. (0.075 mole) of the hydroxydioxolane (VIa), prepared as described above either from Va or from Vc, in 50 cc. of pyridine was added 13 g. (0.114 mole) of methanesulfonyl chloride with swirling. After allowing the mixture to stand at room temperature for 20 minutes, it was poured into an ice-cold sodium carbonate solution. The mesitylate was taken up into ether and the ethereal solution was washed with sodium carbonate solution and water. The residue obtained by concentration of the dried solution was triturated with petroleum ether to give 18.59 g. (81%) of a colorless solid, m.p. 105–106°. Recrystallization from ether yielded the mesylate dioxolane (VIb), m.p. 133–136°, as long colorless prisms. Several recrystallizations from ether, cyclohexane or acetone did not narrow the m.p. range, even though the sample formed well-defined prisms every time: $\lambda_{max}^{CHCl_3}$ 3.35(m), 6.73(w), 6.86(w), 7.05(w), 7.35(s), 7.46(m), 7.64(w), 8.12(w), 8.49(s), 8.86(w), 9.03(m), 9.43(m), 9.75(w), 9.79(w), 10.10(s), 10.27(m), 10.56(s), 11.00(w), 11.22(w) μ.

Anal. Calcd. for $C_{14}H_{24}SO_5$: C, 55.23; H, 7.95; S, 10.53. Found: C, 55.05; H, 7.91; S, 10.53.

Mesylate of *trans*-10-Hydroxymethyl-2-decalone (VIIb).—A solution of 200 mg. of mesylate dioxolane VIb, m.p. 105–106°, in 5 cc. of methanol was warmed with 3 cc. of 10% aqueous hydrochloric acid for 5 minutes. Precipitation with water afforded 135 mg. (79%) of the **keto mesylate VIIb**, m.p. 58–60°. The analytical sample crystallized from ether–petroleum ether as colorless needles, m.p. 61–62°; $\lambda_{max}^{CHCl_3}$ 3.34(m), 5.81(s), 6.73(w), 6.85(w), 7.05(w), 7.33(s), 7.44(s), 7.80(w), 8.11(m), 8.48(s), 8.69(w), 8.88(w), 9.57(w), 9.91(w), 10.13(m), 10.29(m), 10.54(s), 11.65(w) μ.

Anal. Calcd. for $C_{12}H_{20}SO_4$: C, 55.36; H, 7.74; S, 12.31. Found: C, 55.12; H, 7.88; S, 12.72.

The **semicarbazone of the *trans*-keto-mesylate (VIIb)** crystallized from methanol as colorless prisms, m.p. 193–195°.

Anal. Calcd. for $C_{13}H_{23}N_3SO_4$: C, 49.14; H, 7.30; N, 13.24; S, 10.10. Found: C, 49.02; H, 7.26; N, 13.33; S, 10.34.

Sodium Borohydride Reduction of the Keto Mesylate (VIIb).—To a solution of 500 mg. of sodium borohydride in warm absolute methanol was added 500 mg. of the keto mesylate (VIIb), m.p. 58–60°. The mixture was kept warm for 5 minutes and then at room temperature for 30 minutes. Dilution with water, acidification and ether extraction gave the mono-mesylate of ***cis*-10-hydroxymethyl-2-*trans*-decalol (VIIIb)** as an oil which was converted to the benzoate with benzoyl chloride in cold pyridine. Quenching with aqueous sodium carbonate precipitated the benzoate of VIIIb as a colorless solid, m.p. 150–155°, yield 700 mg. (99%). Recrystallization of a sample from ether gave silky colorless needles, m.p. 155–156°.

Anal. Calcd. for $C_{19}H_{26}SO_5$: C, 62.27; H, 7.15; S, 8.75. Found: C, 61.99; H, 7.35; S, 8.90.

Lithium Aluminum Hydride Reduction of the Keto Mesylate (VIIb).—A mixture of 500 mg. of lithium aluminum hydride and 55 cc. of dibutyl ether was refluxed for 30 minutes. After addition of 500 mg. of the keto mesylate (VIIb), m.p. 58–60°, the mixture was refluxed for 12 hours. The excess reagent was decomposed with water and 10% aqueous hydrochloric acid was added until the aqueous layer was clear. The organic solution was separated and dried and the solvent removed at reduced pressure. Crystallization of the residue with ether–petroleum ether yielded 170 mg. (48%) of *cis*-10-hydroxymethyl-2-*trans*-decalol (VIIIa), m.p. 141–142° (reported[5] 141.8–142.6°); $\lambda_{max}^{mineral\ oil}$ 2.95(s), 6.68(w), 7.31(m), 7.41(w), 7.57(w), 7.67(w), 7.87(w), 8.43(w), 8.67(w), 8.89(w), 9.02(w), 9.16(w), 9.44(w), 9.53(s), 9.68(s), 9.99(w), 10.38(m), 10.79(w), 11.61(w), 11.93(w), 12.74(w) μ.

The mother liquor from the crystallization of VIIIa contained an oil with a camphoraceous odor, which would not crystallize. It did not form a crystalline 2,4-dinitrophenylhydrazone nor a 3,5-dinitrobenzoate. This oil may have been the cyclic ether IX.

Reduction of the Dioxolane Mesylate VIb with Lithium in Liquid Ammonia.—To a stirred solution of 500 mg. of the dioxolane mesylate (VIb), m.p. 105–106°, in 100 cc. of refluxing liquid ammonia was added 1 g. of lithium in the form of clean pieces of wire over a period of 45 minutes. (In another experiment with the same result, 3.3 g. of sodium was used instead of lithium.) Absolute alcohol was added dropwise until the blue color had disappeared. The ammonia was removed in a stream of air and the residual solid was taken up in water, neutralized and then acidified with 10 cc. of 10% aqueous hydrochloric acid. After allowing this mixture to stand for 10 minutes at 50°, enough water to bring the volume to 120 cc. was added. The solution was distilled into an excess of 2,4-dinitrophenylhydrazine reagent in 50% aqueous sulfuric acid until no more precipitation occurred in the receiver. The yellow precipitate was filtered to give 170 mg. (30%) of the 2,4-dinitrophenylhydrazone of *trans*-10-methyl-2-decalone (X), m.p. 140–150°. Two recrystallizations from methyl acetate–methanol raised the m.p. to 169–170° and 178–179°, respectively (reported 178–179°[3] and 173–175°[4]). When this sample was mixed with an authentic[4] sample of this derivative of *trans*-10-methyl-2-decalone (X, m.p. 173–175°) the m.p. was 175–178°, while admixture with the derivative of *cis*-10-methyl-2-decalone (m.p. 175–177°)[4] depressed the m.p. to 145–155°.

***trans*-10-Methyl-2-decalone (X).**—To a solution of 5.2 g. of the *trans*-dioxolane mesylate (VIb), m.p. 105–106°, in 50 cc. of dimethylformamide was added 10 cc. of a saturated aqueous solution of sodium hydrogen sulfide (made by passing excess hydrogen sulfide into molten sodium sulfide nonahydrate and decanting from solid)[11] when a gelatinous precipitate formed. When the mixture was refluxed for 12 hours it slowly changed from colorless to blue to green. After standing for 2 days at room temperature, the mixture was poured into a saturated sodium chloride solution and the color disappeared. Ether extraction, drying and concentration produced a pale yellow oil, which was dissolved in 200 cc. of 95% alcohol and stirred in a closed system with Raney nickel catalyst (made from 50 g. of the Raney alloy)[12] for 20 hours at room temperature. The catalyst was filtered, the filtrate was concentrated to 25 cc., treated with

(11) H. Gilman, M. A. Plunkett, L. Tolman, L. Fullhart and H. S. Broadbent, THIS JOURNAL, **67**, 1845 (1945); F. G. Bordwell, B. Pitt and M. Knell, *ibid.*, **73**, 5004 (1951).

(12) A. A. Pavlic and H. Adkins, *ibid.*, **68**, 1471 (1946).

10 cc. of 10% hydrochloric acid at 50° for 10 minutes and allowed to stand at room temperature for 30 minutes. The solution was distilled until no more ketone came over (100 cc. of distillate) and the product was extracted with petroleum ether. Concentration and evaporative distillation at 140–150° (10 mm.) yielded 2.35 g. (82%) of *trans*-10-methyl-2-decalone (X), $n^{24}D$ 1.4872. The 2,4-dinitrophenylhydrazone, which formed in good yield, was recrystallized from methyl acetate–methanol and melted at 178–179° alone and when mixed with this derivative of authentic *trans*-10-methyl-2-decalone.[3,4,13]

(13) We are grateful to Prof. R. B. Woodward for an authentic sample of *trans*-10-methyl-2-decalone which was used to prepare the 2,4-dinitrophenylhydrazone, m.p. 177–178°.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KRISHNAGAR COLLEGE]

Spiro Compounds. 1. Synthesis of 1,2,3,4-Tetrahydronaphthalene-2,2-spiro-(2′-*n*-propylcyclopentane) and Its Rearrangement on Catalytic Dehydrogenation

BY DHIRENDRA NATH CHATTERJEE

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The spirohydrocarbon 1,2,3,4-tetrahydronaphthalene-2,2-spiro-(2′-*n*-propylcyclopentane) (I) has been synthesized in order to study the rearrangement of the alkyl substituted spirocyclopentane ring during dehydrogenation. On dehydrogenation with platinum-on-charcoal at 300–330°, this spiran yielded 1-methylpyrene. The synthesis of the spiran has been effected starting from the anhydride of 2-*n*-propylcyclopentane-1-carboxy-1-acetic acid and benzene.

Dehydrogenation has been an important tool in elucidating the constitution of many natural products, and also has found fruitful application in other fields. The reaction, however, is complicated and attended by side reactions, for the understanding of which a study of the dehydrogenation of a wide range of polynuclear hydroaromatic compounds is desirable. With this end in view, the catalytic dehydrogenation of a particular spiran has been carried out. Selenium dehydrogenation of a large number of spirans had previously been studied by Clemo and Ormston,[1] Cook and Hewett,[2] Levitz and Bogert,[3] Sengupta[4] and others, who had noted ring transformation during dehydrogenation. Recently Sengupta and Chatterjee[5,6] have synthesized a large number of tetralin derivatives containing an alkyl substituted spirocyclopentane ring and studied their catalytic dehydrogenation. They have found that such spirans with a methyl substituent in the spirocyclopentane ring undergo ring transformation during dehydrogenation giving a methylphenanthrene or its derivative. The methyl group present in the spirocyclopentane ring is not eliminated.[5] On the other hand it has been noted by them[6] that the spiran with an ethyl substituent in the spirocyclopentane ring (I, C_2H_5 in place of C_3H_7) on catalytic dehydrogenation under similar conditions yields pyrene. A probable interpretation of this peculiar ring transformation, as occurring through the intermediate formation of a partially reduced 4-ethylphenanthrene and cyclodehydrogenation of the latter, has been given. In order to see whether similar ring transformation takes place with a spiran having a propyl substituent in the spirocyclopentane ring, the spiran 1,2,3,4 - tetrahydronaphthalene - 2,2 - spiro - (2′-*n*-propyl-cyclopentane) (I) has been synthesized by an extension of the method developed earlier.[5] The anhydride of 2-*n*-propylcyclopentane-1-carboxy-1-acetic acid was condensed with benzene in the presence of aluminum chloride to give a single keto acid which has been proved to be α,α-(2′-*n*-propylcyclopentane)-β-benzoylpropionic acid (II). The keto acid reacted with salicylaldehyde in the presence of hydrogen chloride giving a pyrylium salt. This shows the presence of a keto-methylene grouping[7] and as such excludes the alternative structure for the keto-acid. The keto acid II was readily reduced to α,α-(2′-*n*-propylcyclopentane)-γ-phenylbutyric acid (III) by the Clemmensen method. Cyclization of the butyric acid (III) by 85% sulfuric acid afforded 1-keto-1,2,3,4-tetrahydronaphthalene - 2,2 - spiro - (2′ - *n* - propylcyclopentane) (IV). Failure of this ketone to yield a semicarbazone or 2,4-dinitrophenylhydrazone, due to the hindered position of the keto group, lends additional support to the constitution of the keto acid II from which it was derived.[8] On reduction, which was somewhat sluggish, by the Clemmensen method, the spiro-ketone IV afforded the desired spiran I. This on dehydrogenation with 10% platinum-on-charcoal catalyst at 300–330° gave 1-methylpyrene. This is, therefore, in line with the observation made by Sengupta and Chatterjee[6] with respect to the dehydrogenation of the corresponding ethyl substituted spiran, and the same explanation seems probable. The cyclopentane ring undergoes fission near the heavy propyl group with the formation of an intermediate which by angular cyclization forms a partially reduced 4-*n*-propylphenanthrene. This then undergoes cyclodehydrogenation to 1-methylpyrene. Formation of new rings by cyclodehydrogenation under conditions of catalytic dehydrogenation, have been observed by a number of workers,[9,10]

(1) G. R. Clemo and J. Ormston, *J. Chem. Soc.*, 352 (1933).

(2) J. W. Cook and C. L. Hewett, *ibid.*, 365 (1934).

(3) M. Levitz and M. T. Bogert, *J. Org. Chem.*, **8**, 253 (1934).

(4) S. C. Sengupta, *J. Ind. Chem. Soc.*, **11**, 389 (1934); *ibid.*, **16**, 349 (1939); *ibid.*, **17**, 101 (1940).

(5) S. C. Sengupta and D. N. Chatterjee, *ibid.*, **29**, 438 (1952); *ibid.*, **30**, 27 (1953); *ibid.*, **31**, 11 (1954).

(6) S. C. Sengupta and D. N. Chatterjee, *ibid.*, **31**, 285 (1954); *Science and Culture*, **19**, 47 (1953).

(7) (a) W. H. Perkin, Jr., R. Robinson and M. R. Turner, *J. Chem. Soc.*, **93**, 1085 (1908); (b) R. D. Desai and M. A. Wali, *Proc. Ind. Acad. Sci.*, **6A**, 135 (1937).

(8) W. Cocker, B. E. Cross, A. K. Fateen, C. Lipman, E. R. Stuart, W. H. Thompson and D. R. A. Whyte, *J. Chem. Soc.*, 1781 (1950).

(9) W. Baker, J. F. W. Mcomie and J. M. Norman, *ibid.*, 1114 (1951).

(10) B. A. Kazanski and A. F. Plate, *J. Gen. Chem. (U.S.S.R.)*, **9**, 496 (1939).