to that described above, but with a longer period of heating and removal of the acetone by distillation from the steam-cone, the product isolated was a colorless oily base which formed a hydrochloride agreeing in melting point (m.p. 220–222°) with the hydrochloride of ω-morpholinoacetophenone (m.p. 222–223°).[16]

α-Morpholino-β-methoxybenzylacetophenone (VIII).—A solution of 1.5 g. (0.0046 mole) of α-bromo-β-morpholinobenzylacetophenone (III), form B, in 10 ml. of methanol was heated on a steam-cone for 20 minutes. Distilled water was added to precipitate the product, which was removed by filtration, treated with an aqueous sodium bicarbonate solution, collected again by filtration and dried to yield 1 g. (77% yield) of a white solid. After two recrystallizations from petroleum ether (b.p. 65–110°) the compound was obtained as white plates, m.p. 116–117°.

Anal. Calcd. for $C_{20}H_{23}O_3N$: C, 73.82; H, 7.12; N, 4.30. Found: C, 73.67; H, 7.17; N, 4.35.

PITTSBURGH 13, PA.

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[Contribution from the Organic Chemistry Laboratory of the College of Engineering and Technology, Bengal]

Synthesis of 1-Methyl-*trans*-2-decalone and 2,3,4,4a,4b,5,6,7,8,8a,9,10-Dodecahydro-2-phenanthrone

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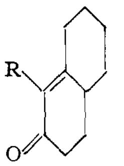
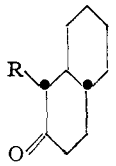
1-Methyl-*trans*-2-decalone (IIa) and *trans*-2-decalone (IIb) have been prepared by the metal–amine reduction of 1-methyl-$\Delta^{1,9}$-2-octalone (Ia) and $\Delta^{1,9}$-2-octalone (Ib), respectively. 2,3,4,4a,4b,5,6,7,8,8a,9,10-Dodecahydro-2-phenanthrone has been prepared from *trans*-2-decalone.

1-Methyl-*trans*-2-decalone (IIa) was obtained first by English and Cavaglieri[3] from decalone, and later by Pinder and Robinson[4] from *trans*-2-decalone. The present synthesis, which is simpler, depends upon the *trans* reduction of 1-methyl-$\Delta^{1,9}$-2-octalone (Ia).



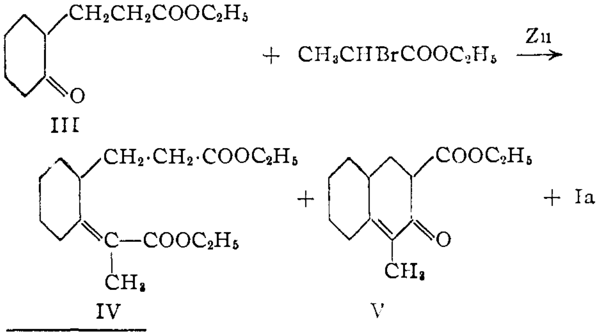
Ia, R = CH_3; Ib, R = H



IIa, R = CH_3; IIb, R = H

Catalytic reduction of polycyclic α,β-unsaturated ketones of type I generally leads to formation of the *cis* isomers of the saturated ketones[5]; however, there are cases in which the *trans* isomer[6] or a mixture of *cis* and *trans* isomers[7] of the reduced ketones has been obtained. Chemical reductions of similar type of compounds, however, have been reported to yield *trans* isomers,[8] the ketones being invariably reduced to secondary alcohols. Recently Djerassi and co-workers[9] reduced a steroidal α,β-unsaturated ketone of the $\Delta^{9,10}$-octalone type to the *trans* isomer without affecting the carbonyl group. They used lithium–amine in the absence of alcohol; in the presence of alcohol the keto group is reduced to a saturated alcohol. With a slight modification of this procedure, Ib and Ia were reduced to IIb and IIa, respectively; the identity of both reduction products was confirmed by comparison with derivatives of authentic specimens. Reduction of Ib by the same method in the presence of alcohol gave *trans*-2-decalol which was oxidized with chromic acid to *trans*-2-decalone. Whereas we obtained only the stable form of the two possible isomers of IIa, Pinder and Robinson[4] obtained a mixture of isomers which on treatment with alkali yielded the homogeneous stable form. According to Barton's conformation rule[10] IIa should represent the configuration of the more stable form in which the C_1-methyl group is equatorial. Catalytic (PtO_2) hydrogenation of IIa in ethanol gave the *cis* isomer, previously prepared by Robinson and Weygand[11] by a different method.

1-Methyl-$\Delta^{1,9}$-2-octalone (Ia) was prepared by condensation[12] of ethyl cyclohexanone-2β-propionate (III) with ethyl α-bromopropionate followed by treatment of the crude condensation product with aqueous alkali. The Reformatsky condensation product, prior to treatment with alkali, consisted of



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[1] Organic Chemistry Department, Indian Institute of Science, Bangalore 3, India.

[2] Indebted to East India Pharmaceutical Works, Ltd., Calcutta, for the award of a fellowship.

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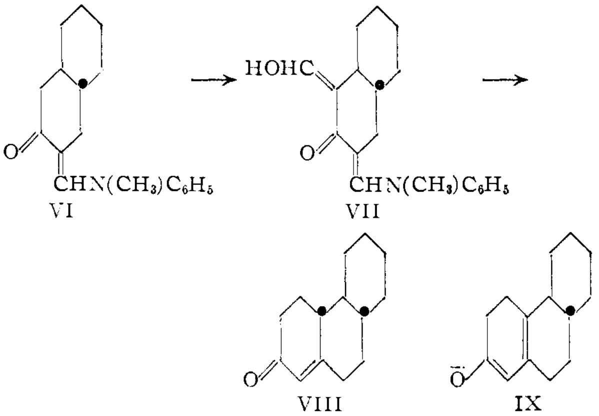
[12] P. S. Adamson, F. C. McQuillin, R. Robinson and J. L. Simonsen, *ibid.*, 1576 (1937).

ethyl 2-β-carbethoxyethylcyclohexylidene-α-propionate (IV), 1-methyl-3-carbethoxy-$\Delta^{1,9}$-2-octalone (V), and Ia; Ia was formed probably by decomposition of V during distillation. $\Delta^{1,9}$-2-Octalone (Ib) was prepared by the Wilds modification[13] of the Robinson–Mannich reaction in a yield higher than that obtained by previous workers.[5a,14]

Because of the high physiological activity of 19-norsteroids[15] it seemed that the preparation of 2,3,4,4a,4b,5,6,7,8,8a,9,10-dodecahydro-2-phenanthrone (VIII) from *trans*-2-decalone through the Robinson–Mannich reaction might be useful. 3-Methylanilinomethylene-*trans*-2-decalone (VI) was prepared by the usual methods[16] for protecting the methylene group. The crude VI was condensed with ethyl formate in the presence of sodium methoxide under benzene and the reaction mixture treated with a methanolic solution of diethylaminobutanone methiodide. The resulting product after treatment with alkali afforded the crystalline unsaturated ketone VIII. The phenanthrene structure of VIII was confirmed by its conversion to phenanthrene. The steric configuration represented by VIII is probably correct because under the reaction conditions isomerization can occur at C_{4a} *via* the common anion IX to give the more stable isomer in which the angular hydrogen at C_{4a} and C_{4b} are polar.



VI VII

VIII IX

Experimental[17]

Ethyl Cyclohexanone-2-β-propionate (III).—This compound was prepared in an improved yield by modifying the procedure of previous workers.[18]

To a stirred solution of 40.8 g. of ethyl cyclohexanone-2-carboxylate in 120 ml. of peroxide-free dioxane was added 2.2 ml. of Triton B followed by a solution of 16 ml. of acrylonitrile in 30 ml. of dioxane. After standing for 12 hours the mixture was treated with a large quantity of dilute hydrochloric acid. The separated oil was extracted with ether and the extract washed with water. After removal of the solvent, 45.4 g. (85%) of ethyl 2-(β-cyanoethyl)-cyclohexanone-2-carboxylate, b.p. 145–150° (1 mm.), was obtained[19]; it was then refluxed for 24 hours with 250 ml. of concentrated hydrochloric acid. The cooled mixture was extracted with ether. The ethereal extract was thoroughly washed with 5% sodium hydroxide solution; the combined alkaline wash was acidified with dilute hydrochloric acid and was extracted with ether–benzene. The crude residue, obtained after thorough removal of the solvent, was refluxed for 20 hours with a mixture of 100 ml. of dry ethanol and 6 ml. of concentrated sulfuric acid, and worked up in the usual manner to give 25 g. (62%) of III, b.p. 115–120° (1.5 mm.).

1-Methyl-$\Delta^{1,9}$-2-octalone (Ia).—To a mixture of 48 g. of III, 44 g. of ethyl α-bromopropionate, and 100 ml. of dry benzene was added 16 g. of zinc wool and a crystal of iodine, and the mixture refluxed for one hour on a steam-bath. A further quantity of 12 g. of zinc and 22 g. of ethyl α-bromopropionate was added and the refluxing continued for another hour. The viscous mass was cooled, treated with cold dilute sulfuric acid and the separated aqueous layer extracted with benzene. The combined extract was washed successively with water, dilute ammonia and water. After removal of the solvent, the residue on fractionation yielded 25 g. of unchanged keto ester III and 16 g. of a residual higher boiling material. The former was treated again with 28 g. of ethyl α-bromopropionate, 10 g. of zinc and 50 ml. of dry benzene and worked up as before. The following fractions were collected during distillation[20] of the combined product: (a) 2 g., b.p. 75–90° (4 mm.); (b) 20 g., b.p. 108–120° (4 mm.); (c) 18 g., b.p. 135–185° (4 mm.); (d) 3 g. of residue.

Fraction c on redistillation yielded 1-methyl-3-carbethoxy-$\Delta^{1,9}$-2-octalone (V), b.p. 135–137° (4 mm.), and ethyl 2-β-carbethoxyethylcyclohexylidene-α-propionate (IV) b.p. 164–167° (4 mm.). The former gave a reddish-brown color with alcoholic ferric chloride. The analytical values indicate that the products were not pure.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.19; H, 8.48. Found: C, 71.10; H, 9.20. Calcd. for $C_{16}H_{26}O_4$: C, 68.08; H, 9.22. Found: C, 67.70; H, 8.70.

Fraction b was mixed with fraction a and refluxed for two hours with 100 ml. of 10% methanolic potassium hydroxide. The cooled alcoholic solution, after dilution with water, was extracted three times with ether. The ether was removed; the residue on distillation yielded 13 g. of 1-methyl-$\Delta^{1,9}$-2-octalone (Ia), b.p. 125–127° (8 mm.); $\lambda_{max.}$ 249 mμ (log E 4.1); colorless oil.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.48; H, 9.76. Found: C, 80.60; H, 9.40.

The semicarbazone, m.p. 212° dec.; $\lambda_{max.}$ 268 mμ (log E 4.5); from alcohol.

Anal. Calcd. for $C_{12}H_{19}N_3O$: N, 19.00. Found: N, 18.75.

A better yield was obtained by employing a longer refluxing time (four hours) and avoiding distillation of the Reformatsky condensation product; the crude condensation product (from 24 g. of ethyl cyclohexanone-2-β-propionate, 33 g. of ethyl α-bromopropionate, 14 g. of zinc wool and 75 ml. of dry benzene) refluxed for four hours with a solution of 25 g. of potassium hydroxide in 250 ml. of water and worked up as before yielded 14 g. (70%) of Ia.

$\Delta^{1,9}$-2-Octalone (Ib).[13]—To a cooled, stirred solution of sodium methoxide (from 3.3 g. of sodium and 125 ml. of dry methanol) was added 17 g. of formylcyclohexanone in an atmosphere of nitrogen, followed by a methanolic solution of diethylaminobutanone methiodide (from 28 g. of diethylaminobutanone, 28 g. of methyl iodide and 300 ml. of dry methanol). The stirring was continued for an hour. After standing overnight, the product was treated with cold dilute hydrochloric acid. The mixture was thoroughly extracted with ether after saturation with ammonium sulfate. The crude residue left after removal of the solvent, was stirred for one hour at 20–22° with 1200

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(17) All melting points are uncorrected.

(18) R. D. Haworth and C. R. Mavin, *J. Chem. Soc.*, 1012 (1933); *cf.* H. T. Openshaw and R. Robinson, *ibid.*, 941 (1937).

(19) This cyanoethylation can be carried out in ordinary dioxane solution with 3 ml. of 50% potassium hydroxide as the condensing agent without impairing the yield; care should be taken to control the vigor of the reaction.

(20) Some decomposition was observed during distillation.

ml. of 2% sodium hydroxide solution in a nitrogen atmosphere. The alkaline solution was thoroughly extracted with ether and the extract dried over sodium sulfate. The solvent was removed and the residue on distillation yielded 13.69 g. (68%) of Ib, b.p. 100-105° (1 mm.), recorded 101–102° (2–3 mm.)[5a]; λ_{max}. 238 mμ (log E 4.1); semicarbazone, m.p. 214° dec., recorded 208°[5a]; 2,4-dinitrophenylhydrazone, m.p. 168° dec., recorded 168°.[5a]

1-Methyl-*trans*-2-decalone (IIa).—To a stirred solution of 2.49 g. of Ia in 15 ml. of dry ether and 15 ml. of purified dioxane, and 900 ml. of anhydrous ammonia was added 0.25 g. of metallic lithium cut into small pieces. The resulting blue solution was stirred for 45 minutes. The blue color did not disappear until most of the ammonia had evaporated. After standing for 20 hours the residual dirty brown mass was diluted with water and extracted three times with ether. The ethereal extract was washed once with water and the solvent removed. Distillation of the residue yielded 1.08 g. (40%)[21] of IIa, b.p. 170–175° (60 mm.), recorded 98° (10 mm.),[3] 110° (11 mm.).[4]

The semicarbazone after one crystallization from ethanol melted at 205–206° dec.; recorded 208-209°,[3] 204–205°.[4] Admixture with an authentic specimen[3] gave no depression of the m.p.

The 2,4-dinitrophenylhydrazone (60% yield) melted in the crude state at 168–170° (shrinking at 165°); recorded 170-171°,[3] 171–172°.[4] After one recrystallization from ethyl acetate the melting points of both the crude product and the authentic specimen[3] rose to a constant value, 179–180° dec.; the mixed m.p. was not depressed.

1-Methyl-*cis*-2-decalone.—A solution of 10.5 g. of Ia in ethanol was shaken with 0.2 g. of platinum oxide catalyst until the calculated amount of hydrogen was absorbed. The reduced ketone was obtained, yield 9 g., b.p. 128–130° (16 mm.), recorded 117–120° (15 mm.).[11]

The semicarbazone after crystallization from ethanol melted at 192.5° dec., recorded 185–191°.[11]

Anal. Calcd. for $C_{12}H_{21}N_3O$: N, 18.84. Found: N, 19.20.

***trans*-2-Decalone (IIb).**—The metal-amine reduction described before, was carried out with a solution of 1.24 g. of Ib in 17 ml. of dry ether and 17 ml. of purified dioxane, 800 ml. of anhydrous ammonia, and 0.14 g. of lithium; 0.8 g. (64%) of IIb was obtained, b.p. 162–164° (60 mm.); recorded 128–129° (23 mm.),[4] 126° (30 mm.).[22] The ether extract was not washed with water in this preparation.

The semicarbazone (90% yield) melted in the crude state at 189–191° dec., recorded m.p. 192–193[22]; the mixed m.p. with an authentic specimen was not depressed. The authentic specimen of *trans*-2-decalone was prepared in 84% yield (75%[4]) by oxidation of *trans*-2-decalol (Merck & Co., Inc.) in benzene solution with a solution of sodium dichromate and sulfuric acid in glacial acetic acid in the cold.

***trans*-2-Decalol.**—To a stirred solution of 2 g. of Ib in 30 ml. of dry ether and 40 ml. of dioxane, and 500 ml. of anhydrous ammonia was added 0.3 g. of lithium. The blue solution was stirred for 13 minutes and then 4.5 ml. of ethanol was added; the blue color was discharged within seven minutes. After removal of ammonia, the residue was diluted with water and extracted with ether. The ether was removed and the residue on distillation yielded 1.02 g. (50%) of *trans*-2-decalol as a colorless oil, which later solidified, m.p. 69-71°; after recrystallization from petroleum ether (40–60°), m.p. 71–72°; the mixed m.p. with an authentic specimen (Merck & Co., Inc., m.p. 75°) was 71–72°.

The recrystallized product (0.5 g. in 8 ml. of benzene) was oxidized with a mixture of 0.32 g. of sodium chromate, 0.63 ml. of acetic acid, 0.45 ml. of concentrated sulfuric acid, and 2 ml. of water in the cold. The crude oily oxidation product was converted to the semicarbazone which was crystallized from ethanol; m.p. 192°, no change of m.p. upon admixture with authentic *trans*-2-decalone.

***trans*-2,3,4,4a,4b,5,6,7,8,8a,9,10-Dodecahydro-2-phenanthrone (VIII).**—To a cooled and stirred suspension of freshly prepared sodium methoxide (from 2.5 g. of sodium) in 20 ml. of dry benzene was added 13 ml. of ethyl formate in an atmosphere of nitrogen followed 15 minutes later by a solution of 8.3 g. of IIb in 20 ml. of dry benzene. After standing overnight, the precipitated sodio salt was dissolved in ice-cold water and the benzene layer extracted thrice with ice-cold 2% potassium hydroxide solution. The combined alkaline solution, after one extraction with ether, was acidified with ice and hydrochloric acid and the mixture extracted four times with ether–benzene. The combined extract was washed once with water and dried over sodium sulfate. The solvent was removed, finally under high vacuum at 100°. A mixture of the crude formylated product, 9.8 g. of monomethylaniline, and 200 ml. of dry benzene was slowly distilled for eight hours. The benzene and unreacted monomethylaniline were completely removed at 50–56° (0.5 mm.). On cooling, the crude methylanilinomethylene (VI) set to a dark colored solid, which was dissolved in 100 ml. of dry benzene and added to a cooled, stirred mixture of 5.1 g. of dry sodium methoxide, 50 ml. of dry benzene and 9 ml. of ethyl formate in an atmosphere of nitrogen. The stirring was continued for two hours. After standing overnight the dark reaction mixture was treated in the cold (ice-bath) with diethylaminobutanone methiodide (from 9.3 g. of diethylaminobutanone), and allowed to stand for 16 hours at room temperature. The mixture was acidified with dilute hydrochloric acid and thoroughly extracted with ether–benzene. The solvent was removed and the residue refluxed for one hour with a solution of 20 g. of potassium hydroxide in 125 ml. of water in a nitrogen atmosphere. The cooled mixture was then extracted three times with ether. The extract was washed with dilute hydrochloric acid and water, and dried over sodium sulfate. The ether was removed and on distillation of the residue, 1.83 g. of unchanged IIb and 2.1 g. (24% over-all yield on the basis of recovered decalone) of an oil, b.p. 136–145° (0.6 mm.), were obtained; the oil solidified on standing, m.p. 70–71°. The recrystallized product melted at 73°, λ_{max}. 239 mμ (log E 4.12).

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.35; H, 9.80. Found: C, 82.43; H, 10.05.

The 2,4-dinitrophenylhydrazone was crystallized from ethanol; m.p. 195–196° dec.

Anal. Calcd. for $C_{20}H_{24}N_4O_4$: N, 14.58. Found: N, 14.73.

Conversion of VIII to Phenanthrene.—A solution of 0.45 g. of the unsaturated ketone VIII in dry ether was slowly added to 0.10 g. of lithium aluminum hydride in 100 ml. of dry ether and the mixture refluxed for two hours. Excess lithium aluminum hydride was decomposed by careful addition of water followed by 20 ml. of ice-cold 10% sulfuric acid. The acidified solution was extracted thoroughly with ether. The residue after removal of the solvent was heated for 15 minutes with 2 g. of potassium bisulfate at 170–175° in an atmosphere of nitrogen and then distilled under vacuum. The oily product was taken up in ether, the solvent removed, and the residue heated for three hours with 30% palladium–charcoal at 250–370° in a Heymann dehydrogenation apparatus. The crystalline sublimate was resublimed with a piece of sodium at 110–120° (0.6 mm.), to yield 200 mg. (50%) of a crystalline product, m.p. 97–99°; picrate, m.p. 143–144°. On admixture with an authentic specimen of phenanthrene and its picrate, the melting points were not depressed.

Acknowledgments.—We are indebted to Professor J. English, Jr., of Yale University for furnishing the 2,4-dinitrophenylhydrazone and semicarbazone of authentic *trans*-2-decalone.

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[21] The yield is improved if the ether extract is not washed with water.

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