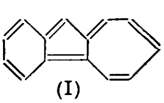
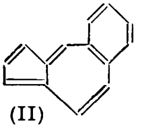
834. *Cyclic Conjugated Polyenes. The Attempted Synthesis of Dehydroindeno*(5′ : 6′-1 : 2)cyclo*heptatriene.*

By A. D. Campbell and S. N. Slater.

Cyclisation of δ-5-indanylvaleric acid gives indano(5′ : 6′-1 : 2)*cyclo*hepten-3-one which is oxidised by selenium dioxide to indano(5′ : 6′-1 : 2)*cyclo*heptene-3 : 4-dione and this on dehydrogenation gives indano(5′ : 6′-α : β)-tropolone. Attempts to dehydrogenate indano(5′ : 6′-1 : 2)*cyclo*hepta-1 : 3-diene, *tricyclo*[7 : 5 : $0^{3:7}$]tetradecane, indano(5′ : 6′-1 : 2)*cyclo*heptene, and 3-methylindano(5′ : 6′-1 : 2)*cyclo*hepta-1 : 3-diene, all prepared from the above monoketone, were unsuccessful.

The existence of the azulenes has served as an incentive in the search for such analogous compounds as pentalene and heptalene but neither of these two substances has yet been prepared. In the azulene series, 1 : 2-benzazulene (I) (Plattner, Fürst, Chopin, and Winteler, *Helv. Chim. Acta*, 1948, **31**, 501; Treibs, *Angew. Chem.*, 1947, **59**, 244; *Ber.*, 1948, **81**, 39; Nunn and Rapson, *J.*, 1949, 825), and 5 : 6-benzazulene (II) (Plattner, Fürst, and Keller, *Helv. Chim. Acta*, 1949, **32**, 2464) are known and Nunn and Rapson (*J.*, 1949, 1051) have prepared a trinitrobenzene complex of 4 : 5-benzazulene (III) although the hydrocarbon itself could not be isolated.


(I)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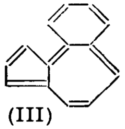
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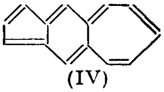
The present communication describes some attempts to prepare dehydroindeno(5′ : 6′-1 : 2)*cyclo*heptatriene (IV) in which the azulene system has been extended by an intermediate six-membered ring. The first route investigated was from 2 : 3-*cyclo*pentenonaphthalene (V) or 5 : 6 : 7 : 8-tetrahydro-5-keto-2 : 3-*cyclo*pentenonaphthalene (VI) (Sen Gupta, *Current Sci.*, 1936, **5**, 133). The most satisfactory preparation of (VI), obtained by cyclisation of γ-5-indanylbutyric acid, was achieved through use of anhydrous hydrogen fluoride as cyclising agent. Although Nunn and Rapson (*loc. cit.*) were successful in enlarging the *cyclo*hexanone ring of 1 : 2 : 3 : 4 : 10 : 11-hexahydrofluoren-3-one with diazomethane, (VI) failed to react with diazomethane even when the latter was generated in the reaction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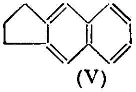
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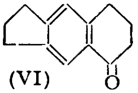
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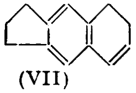
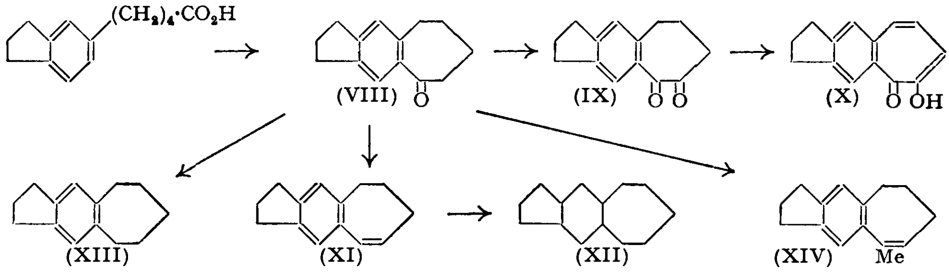

(VII)

mixture (Kohler, Tishler, Potter, and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 1059). The expansion of one of the six-membered rings of fluorene by diazoacetic ester has been described by Plattner *et al.*, by Nunn and Rapson, and by Treibs (*locc. cit.*). A very small yield of condensation product was obtained from (V) and diazoacetic ester, but 5 : 6-dihydro-2 : 3-*cyclo*pentenonaphthalene (VII), obtained from (VI) by reduction with sodium and ethanol and dehydration of the resulting alcohol, reacted with diazoacetic ester to give, after hydrolysis, a crude nitrogen-free acid. This was dehydrogenated with palladium–charcoal and activated alumina. The product was purple, and from it by chromatographic adsorption a small amount of a deep-blue semi-solid was isolated. An attempt to form a trinitrotoluene complex resulted in polymerisation.

The Demjanov reaction provides an alternative method of ring expansion (Plattner, Fürst, and Studer, *Helv. Chim. Acta*, 1947, **30**, 1091) but the necessary methylamino-compound could not be prepared. Hydrogen cyanide failed to react with (VI), and the corresponding alcohol gave only a low yield of the bromide which readily formed (VII) during the attempted preparation of the cyanide.

The next attempt was made from indane by building on a seven-membered ring in a conventional way [indane ⟶ δ-5-indanyl-δ-ketovaleric acid ⟶ δ-5-indanylvaleric acid ⟶ indano(5′ : 6′-1 : 2)*cyclo*hepten-3-one (VIII)]. The position taken up by the entering side-chain in the first reaction was shown by nitric acid oxidation of the product to benzene-1 : 2 : 4-tricarboxylic acid, and the direction of cyclisation by oxidation of the ketone (VIII) to benzene-1 : 2 : 4 : 5-tetracarboxylic acid. The structures of Sen Gupta's products were also confirmed by oxidation of (VI) to the same tetracarboxylic acid. [It should be noted that the trivial names of the benzenetetracarboxylic acids are still a source of confusion in the literature. The correct usage of the trivial names, and the orientation of the acids, is clearly given by Smith and Byrkit (*J. Amer. Chem. Soc.*, 1933, **55**, 4305).]

Oxidation of (VIII) with selenium dioxide gave indano(5′ : 6′-1 : 2)*cyclo*heptene-3 : 4-dione (IX) which was dehydrogenated with palladium–charcoal in boiling trichlorobenzene (Caunt, Crow, Haworth, and Vodoz, *J.*, 1950, 1631) to indano(5′ : 6′-α : β)tropolone (X). A small quantity of the tropolone was also obtained from an oxidation in which the product was distilled from the reaction mixture without previous removal of unchanged selenium dioxide (cf. Borgwardt and Schwenk, *J. Amer. Chem. Soc.*, 1934, **56**, 1185, and Armstrong and Robinson, *J.*, 1934, 1650, for the dehydrogenating action of selenium dioxide). The tropolone gave the usual reactions.



The ketone (VIII) was reduced with sodium and alcohol and the resulting alcohol dehydrated to indano(5′ : 6′-1 : 2)*cyclo*hepta-1 : 3-diene (XI). Because of the possible effect of the degree of hydrogenation on the course of the proposed final dehydrogenation, several related substances were also prepared. Catalytic hydrogenation of (XI) gave the perhydro-derivative *tricyclo*[7 : 5 : $0^{3:7}$]tetradecane (XII), and Clemmensen reduction of (VIII) gave indano(5′ : 6′-1 : 2)*cyclo*heptene (XIII). Methylmagnesium iodide reacted with (VIII) to give the alcohol which lost water on distillation to form 3-methylindano(5′ : 6′-1 : 2)-*cyclo*hepta-1 : 3-diene (XIV).

A wide variety of dehydrogenation techniques (sulphur, selenium, platinum black, palladium–charcoal with and without added solvent, catalytic dehydrogenation in the vapour phase with palladium–charcoal supported on asbestos or with activated alumina, *N*-bromosuccinimide followed by pyridine) was applied to the above substances but in no case was any indication obtained that the desired product was being formed. In most experiments the starting material was recovered or black polymeric products formed. It may well be that the most energetically favoured system possible within the carbon skeleton examined is that in which the central ring is benzenoid, and that for this reason any attempt to prepare (IV) is unlikely to be successful. The situation is, of course, quite different in (I), (II), and (III) where the presence of the benzenoid ring is not incompatible with the development of the fully conjugated cyclic polyene system.

EXPERIMENTAL

5 : 6 : 7 : 8-*Tetrahydro-5-keto-2* : 3-cyclo*pentenonaphthalene* (VI).—γ-5-Indanylbutyric acid (50 g.) and anhydrous hydrogen fluoride (*ca.* 500 g.) were allowed to react for 48 hours. After most of the hydrogen fluoride had evaporated ice was added, and the organic material extracted with ether, washed with water and then aqueous sodium carbonate, dried, and distilled to give the ketone (33 g.), b. p. 190—195°/25 mm. The 2 : 4-*dinitrophenylhydrazone* formed bright red needles (from much acetic acid), m. p. 258° (decomp.) (Found : N, 15·2. $C_{19}H_{18}O_4N_4$ requires N, 15·3%).

5 : 6 : 7 : 8-*Tetrahydro-5-hydroxy-2* : 3-cyclo*pentenonaphthalene.*—Sodium (10 g.) was added in small portions during 2 hours to the above ketone (4·5 g.) in absolute ethanol (70 c.c.), to give the *alcohol* (3·8 g.), b.p. 180—185°/20 mm. (Found : C, 82·7; H, 8·8. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%).

5 : 6-*Dihydro-2* : 3-cyclo*pentenonaphthalene* (VII).—The above alcohol (11 g.) in benzene (20 c.c.) was heated under reflux with phosphoric oxide (13 g.) for 4 hours. The product was poured into water, separated, and distilled, to give the *hydrocarbon* (7 g.), b. p. 148—150°/12 mm. (Found : C, 91·4; H, 8·6. $C_{13}H_{14}$ requires C, 91·8; H, 8·2%).

Attempted Ring-enlargement of 5 : 6-*Dihydro-2* : 3-cyclo*pentenonaphthalene.*—5 : 6-Dihydro-2 : 3-*cyclo*pentenonaphthalene (8·5 g.) was heated to 135—140° and ethyl diazoacetate (5·5 g.) added dropwise with stirring. After 6 hours at this temperature the product was cooled, taken up in ethanol, and then heated under reflux with 30% aqueous potassium hydroxide (10 c.c.) for 2 hours. The solution was cooled, filtered, and diluted with water, and the ethanol distilled off. The residual aqueous solution was washed with ether, and the free acid liberated with 2N-hydrochloric acid, taken up in ether, washed with water, and dried. Evaporation of the ether left the crude acid as a brown sticky nitrogen-free mass (1·4 g.). It was heated under reflux with 30% palladium–charcoal (0·5 g.) and activated alumina (3 g.) for 15 minutes and distilled, to give a pale purple liquid (0·3 g.) boiling over a wide range. This was dissolved in ether and washed with aqueous sodium hydroxide and water, and the ether evaporated, to give a purple residue (0·11 g.). Chromatographic analysis of the oil in *cyclo*hexane on alumina yielded a pale-blue zone from which *cyclo*hexane–benzene (1 : 1) eluted a deep-blue semi-solid (*ca.* 1 mg.).

δ-5-*Indanyl*-δ-*ketovaleric Acid.*—Glutaric anhydride, prepared by heating glutaric acid (25 g.) under reflux with acetic anhydride, in tetrachloroethane (50 c.c.) was added dropwise with stirring to indane (22 g.) in nitrobenzene (50 c.c.) and tetrachloroethane (50 c.c.) containing powdered anhydrous aluminium chloride (57 g.). After 3 hours at room temperature and 15 minutes at 100° the mixture was cooled and poured on ice and hydrochloric acid and then steam-distilled. The residual oil, which solidified on cooling, was filtered off and dissolved in ethanol (charcoal) from which δ-5-*indanyl*-δ-*ketovaleric* acid (30 g.) crystallised as needles, m. p. 103°, after the addition of a small quantity of water (Found : C, 72·1; H, 7·2. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). The *semicarbazone*, crystallised from ethanol, had m. p. 207° (Found : N, 14·4. $C_{15}H_{19}O_3N_3$ requires N, 14·5%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol in bright red needles, m. p. 162·5—163° (Found : N, 13·2. $C_{20}H_{20}O_6N_4$ requires N, 13·6%). Nitric acid oxidation of the keto-acid gave benzene-1 : 2 : 4-tricarboxylic acid, m. p. 215°.

δ-5-*Indanylvaleric Acid.*—The above acid (20 g.) was heated under reflux for 8 hours with amalgamated zinc (30 g.), concentrated hydrochloric acid (140 c.c.), water (60 c.c.), toluene (30 c.c.), and acetic acid (5 c.c.). The toluene layer was separated, the aqueous layer was extracted with ether, and the solvents were removed from the combined extracts. The product was dissolved in 2N-sodium hydroxide, washed with ether, and reprecipitated with mineral acid. Recrystallisation from aqueous ethanol gave δ-5-*indanylvaleric acid* (17 g.), m. p. 70—71° (Found : C, 76·8; H, 8·2. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%).

Indano(5′ : 6′-1 : 2)cyclo*hepten-3-one* (VIII).—The above acid (15 g.) was treated with anhydrous hydrogen fluoride (*ca.* 100 g.). After 24 hours the product was poured on ice, extracted with ether, and washed well with water and aqueous sodium carbonate. Distillation gave the *ketone* as a clear liquid (12 g.), b. p. 200—203°/16 mm. (Found : C, 83·7; H, 7·9. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). The *semicarbazone*, crystallised from ethanol, had m. p. 223° (Found : N, 16·6. $C_{15}H_{19}ON_3$ requires N, 16·3%). The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in deep red needles, m. p. 182—183° (with previous softening when raised slowly from room temperature) (Found : N, 14·7. $C_{20}H_{20}O_4N_4$ requires N, 14·7%). The ketone (0·5 g.) was oxidized with concentrated nitric acid (10 c.c.) at 100° for 3 hours. After the initial vigorous reaction the excess of nitric acid was removed by a slow stream of air. A little water was added and the evaporation to dryness repeated. The residue crystallised from water in clear crystals, sintering at 235° and giving an indefinite m. p. It was esterified with diazomethane, and the methyl ester crystallised from methanol. Hexagonal plates, m. p. 125°, separated and were followed by needles, m. p. 141°, of tetramethyl benzene-1 : 2 : 4 : 5-tetracarboxylate, identical with the product obtained by esterifying the acid from the oxidation of acetyl-ψ-cumene with alkaline potassium permanganate (Mills, *J.*, 1912, 2191). It was at first thought that the substance, m. p. 125°, might be tetramethyl benzene-1 : 2 : 3 : 4-tetracarboxylate (m .p. 133—135°) which would result from the degradation of the ketone with angular fusion of the three rings, but comparison with an authentic specimen, kindly provided by Dr. D. A. Sutton, National Chemical Research Laboratory, Pretoria, showed no similarity. Hexagonal plates, m. p. 125°, giving no depression with the above material of similar m. p., were also isolated from the products of oxidation of acetyl-ψ-cumene. This substance was not further investigated.

Indano(5′ : 6′-1 : 2)cyclo*heptene*-3 : 4-*dione* (IX).—The above ketone (2 g.) in butanol (30 c.c.) was heated under reflux with powdered selenium dioxide (1·7 g.) for 3 hours. The product was cooled, filtered, dissolved in ether, and washed with sodium hydrogen carbonate solution. Distillation gave the *diketone* (1·5 g.), b. p. 195—200°/3 mm. This was dissolved in acetone, centrifuged to remove selenium, and redistilled (Found : C, 78·2; H, 6·9. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%). The 2 : 4 *dinitrophenylhydrazone* crystallised from acetic acid in yellow needles, m. p. 235—236° (Found : N, 13·8. $C_{20}H_{18}O_5N_4$ requires N, 14·2%).

Indano(5′ : 6′-α : β)*tropolone* (X).—(*a*) The diketone (1·2 g.) in 1 : 3 : 5-trichlorobenzene (8 g.) was heated under reflux with palladium–charcoal (0·2 g.; 30%) for 8 hours. The product was diluted with benzene, filtered, and extracted with 2N-sodium hydroxide. The deep yellow alkaline solution was washed with ether and acidified, to give the *tropolone* which crystallised from ethanol in long lemon-yellow crystals (0·08 g.), m. p. 127—128° (Found : C, 78·8, 78·9; H, 5·7, 5·8. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%).

(*b*) Indano(5′ : 6′-1 : 2)*cyclo*hepten-3-one (3 g.) in butanol (60 c.c.) was heated under reflux with selenium dioxide (3·0 g.) for 3 hours. The filtered solution (charcoal) was distilled, having b. p. 170—200°/3 mm. After several weeks, brown crystals of the tropolone (0·3 g.) had separated; they had m. p. 127—128° after crystallisation from ethanol (charcoal). Distillation of the liquid from which the brown crystals had separated gave the diketone (0·5 g.), b. p. 200°/3 mm., together with unchanged starting material.

The tropolone gave a red-brown ferric test, a crimson precipitate when coupled with diazotized *p*-toluidine, and a deep yellow colour in concentrated hydrochloric acid, and was resistant to oxidation with concentrated nitric acid. Oxidation with alkaline potassium permanganate gave benzene-1 : 2 : 4 : 5-tetracarboxylic acid (tetramethyl ester, m. p. 141°).

Indano(5′ : 6′-1 : 2)cyclo*hepten*-3-*ol*.—Indano(5′ : 6′-1 : 2)*cyclo*hepten-3-one (6 g.) in absolute ethanol (100 c.c.) was reduced by addition of sodium (10 g.) during 1 hour. The product was poured into water, and the solid material collected and crystallised from aqueous ethanol, to give the *alcohol* (5·5 g.), m. p. 104° (Found : C, 83·4; H, 8·9. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%).

Indano(5′ : 6′-1 : 2)cyclo*hepta*-1 : 3-*diene* (XI).—The above alcohol (5 g.) was heated with powdered potassium hydrogen sulphate (7 g.) at 180—190° for 2 hours. After cooling, the product was extracted with ether and distilled, to give *indano*(5′ : 6′-1 : 2)cyclo*hepta*-1 : 3-*diene* (3 g.), b. p. 165—168°/17 mm. (Found : C, 90·9; H, 8·7. $C_{14}H_{16}$ requires C, 91·3; H, 8·7%), together with some unchanged starting material.

tricyclo[7 : 5 : $0^{3:7}$]*Tetradecane* (XII).—Indano(5′ : 6′-1 : 2)*cyclo*hepta-1 : 3-diene (10 g.) in acetic acid was hydrogenated at 2 atm. pressure in the presence of Adams's platinum oxide (1·0 g.). After 80 hours no further absorption of hydrogen took place. An oil separated during the hydrogenation. The catalyst was filtered off, and the product poured into water and extracted with ether and *cyclo*hexane. Distillation gave the *hydrocarbon* (8·5 g.) as a clear oily liquid, b. p. 153—155°/15 mm. (Found : C, 87·7; H. 12·2. $C_{14}H_{24}$ requires C, 87·5; H, 12·5%).

Indano(5′ : 6′-1 : 2)cyclo*heptene* (XIII).—Reduction of indano(5′ : 6′-1 : 2)*cyclo*hepten-3-one (11 g.) by the Clemmensen–Martin method for 12 hours yielded the *hydrocarbon* (6 g.) as a clear oil, b. p. 170—172°/16 mm. (Found : C, 89·9; H, 9·4. $C_{14}H_{18}$ requires C, 90·3; H, 9·6%).

3-*Methylindano*(5′ : 6′-1 : 2)cyclo*hepta*-1 : 3-*diene* (XIV).—Indano(5′ : 6′-1 : 2)*cyclo*hepten-3-one (4 g.) in anhydrous ether was added slowly with stirring and cooling to methylmagnesium iodide (from magnesium, 1 g., and methyl iodide, 6 g., in anhydrous ether). The mixture was heated under reflux (2 hours) and then set aside (16 hours) before being decomposed and worked up in the usual way. The alcohol lost water when refluxed at 16 mm., to give the *hydrocarbon* (3·5 g.), b. p. 168°/16 mm. (Found : C, 90·5; H, 9·3. $C_{15}H_{18}$ requires C, 90·9; H, 9·1%).

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