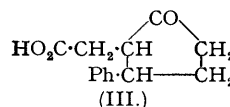
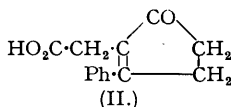
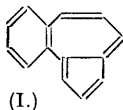


222. Cyclic Conjugated Polyenes. Part II. 4:5-Benzazulene.

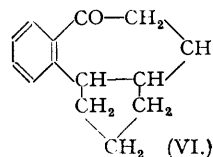
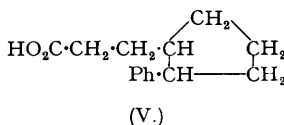
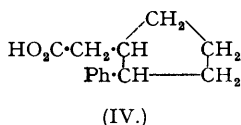
By J. R. NUNN and W. S. RAPSON.

1:2:3:8:9:10-Hexahydro-4:5-benzazulene has been prepared in 6 stages from 3-phenylcyclopent-2-en-1-one-2-acetic acid, and has been dehydrogenated to yield a product characterised as 4:5-benzazulene by the formation of addition compounds with 1:3:5-trinitrobenzene and 2:4:6-trinitrotoluene. In the free state 4:5-benzazulene was found to be unstable. An attempt to prepare a methoxy-4:5-benzazulene via the cyclodehydration of 1-(3-methoxyphenyl-n-propyl)cyclopent-2-one failed.

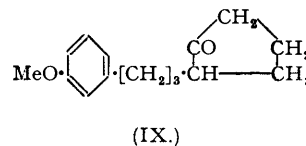
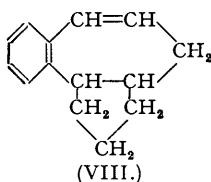
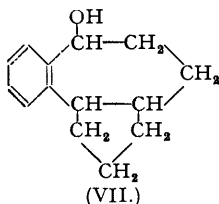
4:5-BENZAZULENE (I), in which a benzene ring is fused to the seven-membered ring of the azulene structure, has been synthesised. For this purpose the ethyl ester of 3-phenylcyclopent-2-en-1-one-2-acetic acid (II) (Robinson, *J.*, 1938, 1390) was hydrogenated, and the acid



(III) derived from the product further reduced by Huang-Minlon's modification of the Wolff-Kishner method (*J. Amer. Chem. Soc.*, 1946, 68, 2487). Attempts to effect the conversion in one stage by application of the Clemmensen method failed, the product under all conditions being a mixture of the derived lactones. 2-Phenylcyclopentane-1-acetic acid (IV) yielded 2-phenylcyclopentane-1-propionic acid (V) in good yield by the Arndt-Eistert method, and the



ring closure of the acid chloride of this acid to yield octahydro-4:5-benzazul-6-one (VI) was carried out in carbon disulphide solution in the presence of aluminium chloride. (VI) afforded the corresponding carbinol (VII) on reduction with sodium and ethanol, and, since the crystalline character of this carbinol caused practical difficulties in its dehydrogenation by the method previously described (Part I, this vol., p. 825), it was dehydrated with potassium hydrogen sulphate to yield the liquid 1:2:3:8:9:10-hexahydro-4:5-benzazulene (VIII). When (VIII), in the vapour phase, was subjected to the action of palladium-charcoal in a vacuum at 350° an intensely blue liquid was produced. A deep blue substance, characterised as 4:5-benzazulene, was extracted from this condensate by means of phosphoric acid, and the unchanged material could be recycled through the dehydrogenation apparatus. In solution 4:5-benzazulene was intensely blue, and it formed well-defined crystalline complexes with



1:3:5-trinitrobenzene and 2:4:6-trinitrotoluene which were very stable and easily obtained in a pure condition. All attempts to obtain this benzazulene in a pure condition for analysis, however, have so far failed. It rapidly underwent change (polymerisation?) to give an insoluble green substance, a reaction which seemed to be catalysed by sunlight. This change occurred even when the operations were carried out under carbon dioxide. This behaviour is in contrast to that of 1:2-benzazulene (Part I, *loc. cit.*) which is a stable compound, and it is intended to attempt the synthesis of 5:6-benzazulene in order to discover whether this instability arises from fusion of the benzene ring to the seven-membered ring of the azulene structure.

Despite its apparent instability, the production of 4:5-benzazulene by a high-temperature dehydrogenation process is indicative of some degree of aromatic character. Further, the

formation and stability of molecular complexes with 1 : 3 : 5-trinitrobenzene and 2 : 4 : 6-trinitrotoluene indicate that the 4 : 5-benzazulene structure has high polarisability and hence considerable electron mobility. The effects of polarising substituents on the stability of 4 : 5-benzazulene are worthy of further study, and experiments are planned from this point of view.

In an attempt to synthesise a methoxy-4 : 5-benzazulene and at the same time to elaborate another 4 : 5-benzazulene synthesis, the cyclodehydration of 1-(3-*m*-methoxyphenyl-*n*-propyl)-cyclopentan-2-one (IX) has been explored. 3-*m*-Methoxyphenyl-*n*-propyl iodide, prepared according to the directions of Robinson and Schlittler (*J.*, 1935, 1288), was condensed with ethyl potassiumcyclopentan-2-one-1-carboxylate to give a high yield of 1-carbethoxy-1-(3-*m*-methoxyphenyl-*n*-propyl)cyclopentan-2-one. This substance was hydrolysed with barium hydroxide to give 1-(3-*m*-methoxyphenyl-*n*-propyl)adipic acid, which would not crystallise. When this acid was distilled in the presence of barium hydroxide it afforded 1-(3-*m*-methoxyphenyl-*n*-propyl)cyclopentan-2-one (IX).

The action of phosphoric oxide on (IX) in boiling benzene or toluene produced no change. When, however, this substance was subjected to prolonged treatment with phosphoric oxide, in boiling xylene, a hydrocarbon was isolated. The analysis and physical constants made it difficult to decide between the formulæ $C_{14}H_{22}$ and $C_{15}H_{24}$.

It is certain that it contained a benzene nucleus since :

(a) The ultra-violet absorption spectrum shows an intense maximum ($\log \epsilon$ 3.13) at 352 μ . Benzene and all alkylated benzenes have their maxima in this region (Baly and Collie, *J.*, 1905, 87, 1332).

(b) In a series of test-tube reactions the hydrocarbon was nitrated and the nitro-compound, so formed, reduced to the corresponding amine. When this amine was diazotised and the diazo-solution added to a strongly alkaline solution of β -naphthol, a deep red colour developed, which could only have occurred had the original substance contained a benzene nucleus.

Despite these observations, however, no characteristic product was obtained in attempts to degrade it with either potassium permanganate or chromic oxide and this substance remains unidentified.

Arylcyclopentenoneacetic acids such as (II) appear to constitute more convenient starting materials for the preparation of substituted 4 : 5-benzazulenes.

EXPERIMENTAL.

(M. p.s are uncorrected.)

3-Phenylcyclopentan-1-one-2-acetic Acid (III).—3-Phenylcyclopent-2-en-1-one-2-acetic acid (135 g.) (Robinson, *loc. cit.*) was esterified by refluxing in absolute ethanol (500 c.c.), containing sulphuric acid (15 c.c.), for 4 hours. On being worked up the mixture afforded the ester (126 g.), b. p. 166—167°/0.5 mm., which solidified on standing. Recrystallisation from light petroleum (b. p. 30—50°) gave large colourless prisms with a hexagonal cross-section, m. p. 46—47° (Found : C, 73.7; H, 6.7. $C_{15}H_{18}O_3$ requires C, 73.8; H, 6.6%). This ester (126 g.) was hydrogenated in ethanol solution in the presence of palladium-calcium carbonate catalyst. Removal of the catalyst and distillation afforded 3-phenylcyclopentan-1-one-2-acetate (126 g.) as an oil, b. p. 160—162°/1 mm., $n_D^{15.3}$ 1.5234 (Found : C, 73.0; H, 7.2. $C_{15}H_{18}O_3$ requires C, 73.2; H, 7.3%). Hydrolysis of this ester yielded 3-phenylcyclopentan-1-one-2-acetic acid (111 g.) as an oil which solidified on standing. Recrystallisation from light petroleum (b. p. 50—60°) gave stout colourless prisms, m. p. 129—130° with softening at 120° (Found : C, 71.8; H, 6.5. $C_{13}H_{14}O_3$ requires C, 71.5; H, 6.5%).

2-Phenylcyclopentane-1-acetic Acid (IV).—A solution of 3-phenylcyclopentan-1-one-2-acetic acid (55 g., 0.25 mol.), potassium hydroxide (42.4 g., 0.76 mol.) and 50% (w/w) hydrazine hydrate (59 c.c.) in 2 : 2'-dihydroxydiethyl ether (310 c.c.) was refluxed for 1.5 hours. At the end of this period the condenser was removed and enough water distilled off to raise the temperature of the solution to 195—200°, where it was maintained for 3 hours. The cooled liquor was then poured into water, acidified, and the liquid acid (49 g.) extracted with ether. For the purpose of characterisation a small quantity of this acid was esterified with ethanol containing a trace of sulphuric acid to give the ethyl ester, b. p. 119—121°/0.5 mm. (Found : C, 77.9; H, 8.4. $C_{15}H_{20}O_2$ requires C, 77.6; H, 8.6%).

2-Phenylcyclopentane-1-propionic Acid (V).—Phosphorus pentachloride (8.2 g., 0.038 mol.) was added to a solution of 2-phenylcyclopentane-1-acetic acid (7.8 g., 0.038 mol.) in dry benzene (85 c.c.). The mixture was stirred till solution was complete and then the benzene and phosphorus oxychloride were distilled off under vacuum on the water-bath. Distillation of the residue afforded the acid chloride (6.3 g.), b. p. 120—122°/0.1 mm. This acid chloride (6.3 g., 0.028 mol.), in a little ether, was added dropwise to a vigorously-stirred anhydrous solution of diazomethane (3.6 g., 0.085 mol.) in ether which was kept between -5° and 0° . A vigorous evolution of nitrogen began immediately, and after standing for half an hour at this temperature the solution was allowed to warm to room temperature and then set aside overnight. The next morning the ether and excess diazomethane were removed under reduced pressure on a water-bath kept initially at 20° and finally at 30°, leaving a viscous yellow residue of diazo-ketone, which was dissolved in absolute ethanol (75 c.c.) and warmed on a water-bath kept at 80°.

A slurry of silver oxide, obtained from 10% silver nitrate solution (12 c.c.), in absolute ethanol (30 c.c.) was then added, in 6 equal portions, to the solution of diazoketone over a period of 2 hours. The solution was then refluxed gently for half an hour, but even after this treatment some unreacted diazoketone remained. Reaction was complete after the solution had been left overnight. A little charcoal was added to the mixture which was then boiled and filtered hot. Distillation gave *ethyl 2-phenylcyclopentane-1-propionate* (6.0 g., 86% of theory calculated on acid chloride), b. p. 132—133°/0.4 mm., n_D^{20} 1.5140 (Found : C, 77.8; H, 8.6. $C_{18}H_{22}O_2$ requires C, 78.0; H, 8.9%). Hydrolysis of this ester gave the acid as pale yellow plates from light petroleum (b. p. 30—50°), m. p. 77—78° (softens 76°) (Found : C, 76.9; H, 8.2. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.3%).

Octahydro-4 : 5-benzazol-6-one (VI).—The acid chloride of 2-phenylcyclopentane-1-propionic acid was prepared by adding the acid (45 g., 0.2 mol.) in dry benzene (200 c.c.) dropwise to a vigorously-stirred solution of phosphorus pentachloride (43 g., 0.2 mol.) in dry benzene (300 c.c.). The benzene and phosphorus oxychloride were then removed under reduced pressure with heating on a water-bath. In order to remove the last trace of phosphorus oxychloride a further 20 c.c. of benzene was added and again removed under reduced pressure. This acid chloride, in pure carbon disulphide (400 c.c.), was added dropwise to a vigorously-stirred mixture of finely-ground aluminium chloride (30.4 g.) and carbon disulphide (2400 c.c.) over a period of 6 hours, the solution being in a bath kept at 40—50°. After all the acid chloride had been added the mixture was refluxed for a further 3 hours. The dark red-brown carbon disulphide solution was then poured on crushed ice and hydrochloric acid. The undissolved complex in the flask was similarly treated and the ketone extracted from it with ether. The combined extracts were then washed with alkali and water and dried (Na_2SO_4). Evaporation of the solvent and distillation of the residue yielded the *ketone* (28 g., 68% of theory calculated on acid) as an oil, b. p. 126—127°/0.2 mm., which immediately solidified. Recrystallisation from light petroleum (b. p. 20—40°) gave clusters of needles, m. p. 65.5—67° with previous softening (Found : C, 84.55; H, 8.1. $C_{14}H_{16}O$ requires C, 84.0; H, 8.1%). The *semicarbazone* separated from ethyl acetate in well-formed colourless plates, m. p. 202—204° (Found : C, 70.2; H, 7.35. $C_{15}H_{18}ON_3$ requires C, 70.0; H, 7.4%).

Octahydro-4 : 5-benzazol-6-ol (VII).—Sodium (16.3 g.) was added in small pieces over a period of an hour to a boiling solution of octahydro-4 : 5-benzazol-6-one (16.3 g.) in absolute ethanol (163 c.c.). When all the sodium had dissolved the solution was cooled, diluted with water, and the carbinol isolated by means of ether. The dried neutral extract yielded, on distillation, *octahydro-4 : 5-benzazol-6-ol* (11.23 g.) as a very viscous colourless oil, b. p. 120—125°/0.2 mm., which crystallised on standing. It gave very fine, colourless needles from light petroleum (b. p. 50—60°), m. p. 119—119.5° (softens 110°) (Found : C, 82.7; H, 9.0. $C_{14}H_{18}O$ requires C, 83.1; H, 9.0%).

1 : 2 : 3 : 8 : 9 : 10-*Hexahydro-4 : 5-benzazulene* (VIII).—Octahydro-4 : 5-benzazol-6-ol (3.0 g.) was heated with potassium hydrogen sulphate (4.3 g.) at 180—190° for 1.5 hours. The mixture was then cooled, extracted with ether, and the ethereal solution washed with alkali and water and dried. Distillation of this extract gave a colourless oil, b. p. 99—100°/0.2 mm., n_D^{20} 1.5818, d_4^{20} 1.018, $[R]_D^{20}$ 60.34 (calc. 58.38) (Found : C, 90.5; H, 8.7. $C_{14}H_{16}$ requires C, 91.3; H, 8.7%).

Dehydrogenation of Hexahydro-4 : 5-benzazulene.—The apparatus and procedure previously described (Part I, *loc. cit.*) were used to dehydrogenate this hydrocarbon. The optimum temperature was 350°. The deep blue distillate from the reaction was taken up in light petroleum (b. p. 20—40°) and extracted with ice-cold 85% phosphoric acid. This phosphoric acid extract was yellow and displayed an intense green fluorescence. After being thoroughly washed with ice-cold petroleum, the phosphoric acid extract was poured into a mixture of ice and peroxide-free ether. Evaporation of the solvent from the dry neutral ethereal solution afforded 4 : 5-benzazulene as a viscous blue oil. The petroleum solution (after the phosphoric acid extraction) was washed and dried and the solvent evaporated. The residue was then subjected to further dehydrogenation. Proceeding in this fashion 6.7 g. of hexahydrobenzazulene afforded, by successively extracting and recycling, 1.86 g. of crude 4 : 5-benzazulene. The 1 : 3 : 5-*trinitrobenzene* addition compound separated from ethanol in deep brown needles, m. p. 160—161° (Found : C, 61.9; H, 3.5. $C_{20}H_{13}O_6N_3$ requires C, 61.4; H, 3.35%). The 2 : 4 : 6-*trinitrotoluene* addition compound separated from ethanol in black-brown needles, m. p. 120° (Found : C, 62.7; H, 4.15. $C_{21}H_{15}O_6N_3$ requires C, 62.2; H, 3.7%).

1-*Carbethoxy-1-(3-m-methoxyphenyl-n-propyl)cyclopentan-2-one*.—3-*m*-Methoxyphenyl-*n*-propyl iodide (20 g.), prepared according to Robinson and Schlittler (*loc. cit.*), was added to ethyl potassium-cyclopentan-2-onecarboxylate, prepared from powdered potassium (2.8 g.) and keto-ester (11.6 g.) in xylene (100 c.c.), and the mixture refluxed for 8 hours. The well washed and dried xylene solution was distilled, affording a colourless product (15 g., 70%), b. p. 165—170°/0.1 mm., n_D^{20} 1.5180. The *semicarbazone* separated from ethanol in colourless plates, m. p. 126° (Found : C, 63.5; H, 7.8. $C_{19}H_{27}O_4N_3$ requires C, 63.2; H, 7.5%).

1-(3-*m*-Methoxyphenyl-*n*-propyl)cyclopentan-2-one (IX).—1-Carbethoxy-1-(3-*m*-methoxyphenyl-*n*-propyl)cyclopentan-2-one (25.5 g.), barium hydroxide (80 g.), and water (150 c.c.) were refluxed for 12 hours. After cooling the mixture was acidified and allowed to stand overnight in order completely to decompose the barium salt. The acid, isolated by ether extraction followed by evaporation of the ether, was an uncrystallisable oil. It was mixed with powdered barium hydroxide (1 g.) and distilled slowly at atmospheric pressure. The distillate, in ether, was washed with alkali and water and dried, the ether evaporated, and the residue distilled, affording an oil (13.1 g.), b. p. 151—180°/0.4 mm., n_D^{20} 1.5307. The *semicarbazone* crystallised from ethanol in colourless feathery needles, m. p. 173° (Found : C, 66.3; H, 7.8. $C_{16}H_{23}O_2N_3$ requires C, 66.4; H, 8.0%).

The Action of Phosphoric Oxide on 1-(3-m-Methoxyphenyl-n-propyl)cyclopentan-2-one.—The material was recovered unchanged after refluxing in toluene solution with additions of phosphoric oxide over a period of 3 hours. This recovered material (10.8 g.) in xylene (400 c.c.) was refluxed, with periodic additions of phosphoric oxide, for 50 hours. The sticky brown complex remaining after pouring off the xylene solution was treated with excess of alkali and extracted with ether. The combined ethereal extract and xylene solution were washed, dried, and distilled, affording a main fraction, b. p. 120—

123°/0.1 mm. This was redistilled, giving a colourless oil (3.5 g.), b. p. 104—107°/0.2 mm. (Found : C, 88.4; H, 11.4%). Distillation over sodium did not effect any change, b. p. 107—109°/0.2 mm., n_D^{20} 1.5042, d_4^{20} 0.927, $[R]_D$ 66.40 [Found : C, 88.2; H, 11.3%; M (Rast), 208. $C_{14}H_{22}$ requires C, 88.3; H, 11.6%; $[R]_D$ (for 3 double bonds), 61.25; M , 190. $C_{15}H_{24}$ requires C, 88.2; H, 11.8%; $[R]_D$ (for 3 double bonds), 65.87; M , 204].

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