

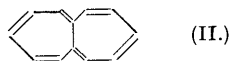
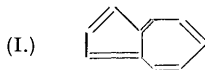
178. Cyclic Conjugated Polyenes. Part I. 1:2-Benzazulene.

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

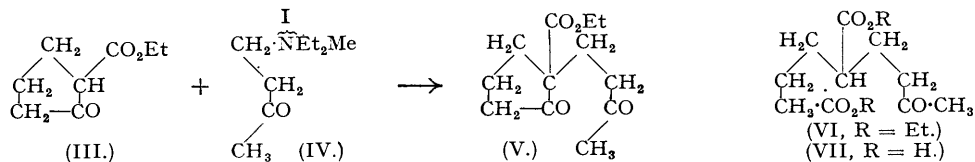
1:2-Benzazulene has been synthesised by two methods. The first method is an extension of an azulene synthesis based upon the ring expansion of hexahydroindan-5-one with diazomethane to yield decahydroazulones which are reduced and dehydrogenated to yield the azulenes themselves. The second method is an application of St. Pfau and Plattner's azulene synthesis (*Helv. Chim. Acta*, 1939, **22**, 202) which begins with the action of diazoacetic ester on fluorene. 1:2-Benzazulene is a deeply coloured, stable, crystalline substance showing many of the attributes of the azulenes themselves. It has been characterised by the formation of molecular complexes with 1:3:5-trinitrobenzene and 2:4:6-trinitrotoluene, and as a first step in its physical examination its visible and ultra-violet absorption spectra are recorded.

In view of the interest that has been focussed for so many years on the problem of the structure and stability of benzenoid compounds, it is perhaps surprising that so little attention has been paid to analogous cyclic conjugated polyene structures, some of which may constitute new aromatic types (cf. Baker, *J.*, 1945, 258). Amongst such structures, that of azulene (I) is of particular interest, but although much attention has been paid to the synthesis and examination of it and its derivatives, no compound containing a benzene ring fused to an azulene has as yet been described. Cook, McGinnis, and Mitchell (*J.*, 1944, 286) have, however, recorded unsuccessful attempts to produce 5:6-benzazulene by dehydrogenation.

1:2-Benzazulene has now been synthesised by two methods. The first of these is an extension of an azulene synthesis which was designed to serve as a model not only for this preparation but also for that of heptalene (*bicyclo*[5:5:0]dodecahexaene) (II), through the use of *cyclo*-heptanone as starting material.

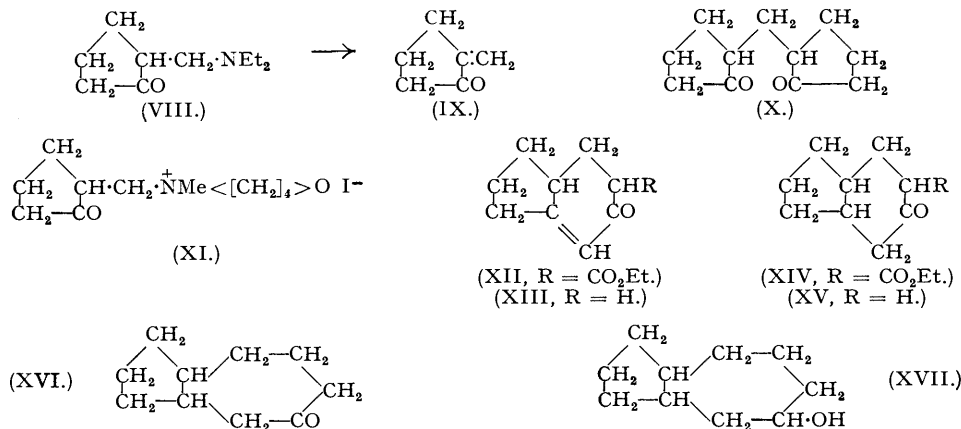


The Azulene Synthesis.—Two alternative methods for the preparation of the hexahydroindan-5-one (XV), required for the azulene synthesis, were explored. When the condensation of ethyl *cyclopentan-2-one-1-carboxylate* (III) with 4-diethylaminobutan-2-one methiodide (IV) was carried out in ethanol solution at the boiling point, in the presence of sodium ethoxide, a neutral substance $C_{14}H_{24}O_5$ was isolated. This has been formulated as (VI):



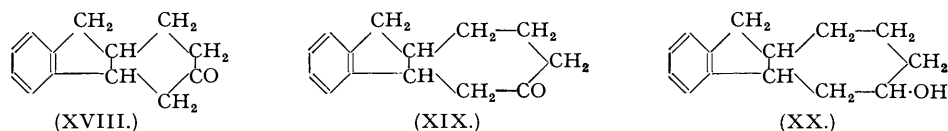
The action of alcoholic alkali on this latter substance (VI) produced a liquid acid which, on the evidence of the saponification equivalent of its *diethyl* ester, was considered to be α -butan-3-onyladipic acid (VII). That the formation of (VI) occurred through the intermediate formation of (V) was indicated by the isolation of 2-carbethoxy-2-butan-3'-onylcyclopentanone (V) when the condensation was carried out in ethanol at 0°. This compound (V) was also produced when the reaction was carried out in an inert medium (benzene) but no conditions were found for its cyclisation and hydrolysis to (XIII). These results are similar to those obtained by Rapson (*J.*, 1936, 1626) by the reaction of ethyl *cyclopentan-2-one-1-carboxylate* with $\alpha\beta$ -unsaturated ketones. In the alternative and successful route the Mannich base from *cyclopentanone*, formaldehyde, and morpholine was preferable to that from acetone, formaldehyde, and diethylamine. However, before morpholine was used, an attempt was made to prepare the Mannich base (VIII) from

diethylamine. From the reaction between *cyclopentanone*, diethylamine hydrochloride, and formaldehyde two substances were isolated. The first one, a low-boiling oil, had the formula, C_6H_8O , and has been formulated as 2-methylene*cyclopentanone* (IX) since it gave 2-methyl*cyclopentanone* on hydrogenation in the presence of palladium-calcium carbonate catalyst. The second substance, a high-boiling, viscous oil was a diketone of the formula $C_{11}H_{16}O_2$, which is formulated as bis*cyclopentan-2-onylmethane* (X). The formation of these substances is attributed to the instability of the Mannich base (VIII) which is presumably a first product under the conditions of reactions used. 2-Diethylaminocyclopentanone (VIII) has been recorded subsequently to this work (Skoda, *Bull. Soc. chim.*, 1946, 328) but we have not had access to a description of the conditions used.



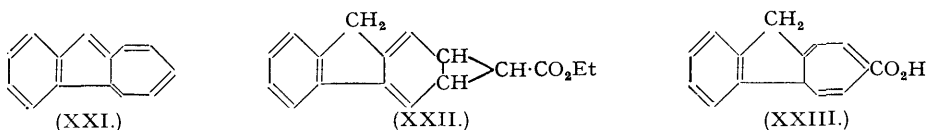
The condensation between 2-(morpholinomethyl)cyclopentanone methiodide (XI) and acetoacetic ester in anhydrous ethanol in the presence of sodium ethoxide proceeded smoothly to give a good yield of 6-carbethoxy-5 : 6 : 7 : 8-tetrahydroindan-5-one (XII) in two diastereoisomeric forms. Hydrogenation of the mixture gave 6-carbethoxyhexahydroindan-5-one (XIV, mixed isomers), hydrolysis of which was carried out by heating at 180—190° with glycerol, containing 10% of water (cf. du Feu, McQuillin, and Robinson, *J.*, 1937, 53), to give hexahydroindan-5-one (XV, mixed isomers) in moderate yield. The results obtained in the ring expansion of this substance with diazomethane accord with those reported by Plattner, Fürst, and Studer (*Helv. Chim. Acta*, 1947, 30, 1091) some months after the present work was completed. No epoxide was isolated, but a mixture of the semicarbazones of the isomeric bicyclo[5 : 3 : 0]decan-3-ones (XVI) was formed directly from the reaction mixture, and was separated into its constituents. The reduction of the ketones derived from these semicarbazones to yield a stereoisomeric mixture of bicyclo[5 : 3 : 0]decan-3-ols (XVII) presented no difficulty. The dehydrogenation of this carbinol was carried out in a vacuum at 300—350° over a palladium-charcoal catalyst using an apparatus specially designed for this purpose. The intensely blue distillate was proved to be azulene by conversion into the known 2 : 4 : 6-trinitrotoluene derivative.

1 : 2-Benzazulene. *First Method.*—For the synthesis of 1 : 2-benzazulene, 1 : 2 : 3 : 4 : 10 : 11-hexahydrofluoren-3-one (XVIII) was prepared from indan-1-one by a cyclohexenone synthesis (Harradence and Lions, *J. Proc. Roy. Soc. New South Wales*, 1939, 72, 284) and submitted to the action of diazomethane to give a mixture of ketones formulated as 9 : 10-benzbicyclo[5 : 3 : 0]dec-9-en-3-one (XIX, mixed isomers) by analogy with the products of the reaction previously described. Neither the mixed semicarbazones nor the mixed oximes of this ketone could be



induced to crystallise, but the 2 : 4-dinitrophenylhydrazones crystallised well. The reduction of the ketone (XIX, mixed isomers) with sodium and ethanol, proceeded smoothly to give 9 : 10-benzbicyclo[5 : 3 : 0]dec-9-en-3-ol (XX, mixed isomers), which was an extremely viscous liquid. The value of the dehydrogenation apparatus previously mentioned is particularly clear

in this case. An attempt to dehydrogenate the carbinol (XX) by heating it with sulphur at 200—220° resulted in polymerisation. Heating with palladium-charcoal and passing over palladium-charcoal at 300—350° in the vapour phase were equally ineffective in promoting dehydrogenation. When, however, the previously mentioned vacuum-dehydrogenation technique was used, a comparatively high yield of 1 : 2-benzazulene (XXI) was realised. Whenever new catalyst was used in this dehydrogenation the first few drops of distillate consisted of a colourless crystalline substance (m. p. 94—97°). Investigation of this compound was not possible as only a very few milligrams were produced in all, but the m. p. indicated that it might have been phenanthrene (m. p. 99°) formed by rearrangement of 1 : 2-benzazulene



[cf. the rearrangement of azulene to naphthalene in a vacuum under the influence of heat (Heilbronner and Wieland, *Helv. Chim. Acta*, 1947, 30, 947)]. Like other azulenes 1 : 2-benzazulene was found to be soluble in 85% phosphoric acid, from which it could be regenerated by

FIG. 1.
Ultra-violet absorption curves of
1 : 2-benzazulene (—) and azulene (·-·-·).

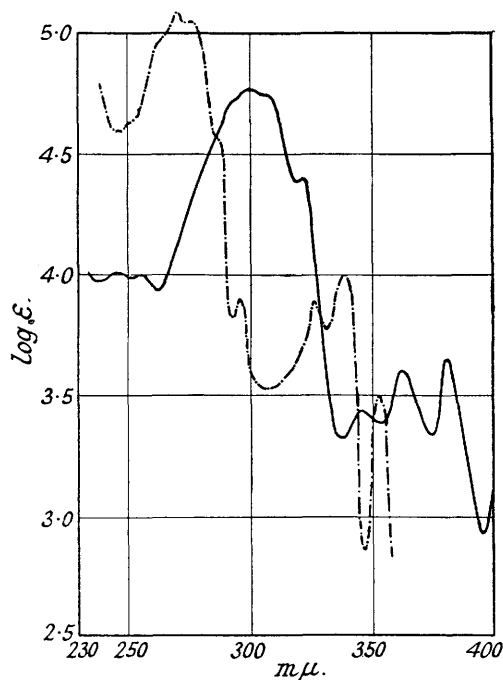
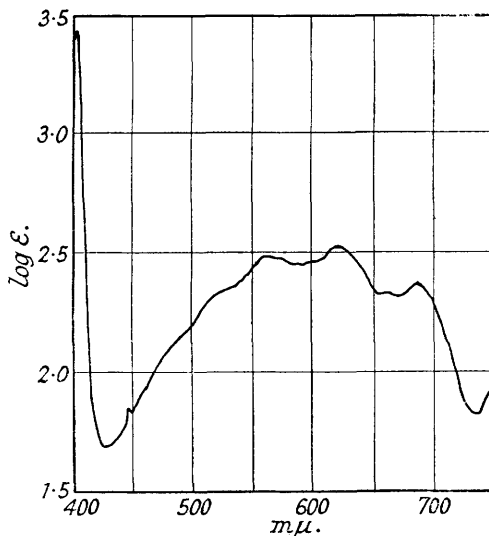


FIG. 2.
Visible absorption curve of 1 : 2-benzazulene.



the addition of ice-cold water. Making use of this property the azulene was extracted from the crude dehydrogenation product, that part of the reaction mixture insoluble in phosphoric acid being recycled through the apparatus to give more benzazulene. It formed well-defined, highly-crystalline and deeply-coloured complexes with both 2 : 4 : 6-trinitrotoluene and 1 : 3 : 5-trinitrobenzene. The pure hydrocarbon was obtained from either of these complexes by decomposing the complex on a column of alumina (cf. Plattner and St. Pfau, *Helv. Chim. Acta*, 1937, 20, 224). The hydrocarbon crystallised from ethanol in deep green plates, which sublimed somewhat below the melting point and decomposed slowly on melting. In solution it exhibited an intense blue colour with a faint tinge of red at certain dilutions. The ultra-violet absorption spectrum (Fig. 1) shows a very marked resemblance to that of azulene which is given

in the same diagram. The visible absorption spectrum (Fig. 2) is typical of the azulenes, the absorption maxima being, in general, very broad bands.

1:2-Benzazulene. *Second Method* (with D. H. S. HORN).*—The reaction of diazoacetic ester with fluorene (cf. St. Pfau and Plattner, *Helv. Chim. Acta*, 1939, **22**, 202) gave a condensation product formulated as (XXII), hydrolysis of which yielded the acid (XXIII). When this acid was distilled in a vacuum over palladium-charcoal a high yield of 1:2-benzazulene was obtained. This synthesis is being exploited as a mode of access to 1:2-benzazulene and its derivatives in quantities sufficient for an examination of their chemical properties.

EXPERIMENTAL.

(M. p.s are uncorrected.)

Condensation of Ethyl Sodiocyclopentan-2-one-1-carboxylate with 4-Diethylaminobutan-2-one.—(a) *In boiling ethanol.* A solution of sodium ethoxide, which had been prepared by dissolving sodium (3.9 g., 0.17 atom) in anhydrous ethanol (300 c.c.), and ethyl cyclopentan-2-one-1-carboxylate (31.2 g., 0.2 mol.) was cooled in ice. 4-Diethylaminobutan-2-one methiodide (40 g., 0.14 mol.), prepared according to the method of du Feu, McQuillin, and Robinson (*J.*, 1937, 56), in anhydrous ethanol (120 c.c.) was then added dropwise. After one hour the solution was heated under reflux for 3 hours, cooled, and mixed with water and ether. The ether was evaporated from the dried, neutral extract, and the residue distilled giving unchanged ethyl cyclopentanonecarboxylate (7.5 g.), b. p. 90–100°/0.1 mm., and a fraction (24 g.), b. p. 100–144°/0.1 mm. Redistillation of this latter fraction yielded an oil (15.4 g.), n_D^{25} 1.4438, b. p. 143–149°/0.1 mm. (Found: C, 61.2, 61.8; H, 8.8, 8.8. $C_{14}H_{24}O_5$ requires C, 61.7; H, 8.8%). This substance which has been formulated as *diethyl α -butan-3-onyladipate* (VI) gave no ketonic reactions, but gave a positive iodoform reaction. This behaviour is in accordance with the behaviour of analogous compounds isolated by Rapson (*loc. cit.*). Saponification of this ester with alcoholic alkali yielded an acid which could not be induced to crystallise. Re-esterification of this acid with ethanol, containing a trace of sulphuric acid, gave an ester, b. p. 140°/0.1 mm. [Found: equiv., 138.7 (by saponification). Calc. for $C_{14}H_{24}O_5$: equiv., 136].

(b) *In ethanol at 0°.* Sodium (3.9 g., 0.17 atom), dissolved in anhydrous ethanol (300 c.c.) and cooled in ice, was treated with ethyl cyclopentan-2-one-1-carboxylate (39 g., 0.25 mol.). 4-Diethylaminobutan-2-one methiodide (49 g., 0.17 mol.) in anhydrous ethanol (100 c.c.) was then added dropwise, with cooling in ice and constant swirling. After 17 hours at 0° the mixture was diluted with water and extracted with ether. Extraction of the ethereal layer with sodium hydrogen carbonate yielded, on acidification, a negligible trace of a liquid acid. The washed and dried ethereal solution was then distilled, using a short column. The first fraction (7.6 g.), b. p. 75–80°/0.1 mm., consisted of unchanged ethyl cyclopentanonecarboxylate. It was followed by a mixed fraction (6.0 g.), b. p. 80–115°/0.1 mm., and a fraction (11.6 g.), b. p. 115–120°/0.1 mm. (Found for last fraction: C, 63.4; H, 7.9. $C_{12}H_{18}O_4$ requires C, 63.7; H, 7.9%). The *disemicarbazone* of this fraction separated from aqueous ethanol in colourless, flattened needles, m. p. 178–179° (decomp.) (Found: C, 49.15; H, 7.3. $C_{14}H_{24}O_4N_2$ requires C, 49.4; H, 7.1%). This substance is considered to be 2-carbethoxy-2-butan-3'-onylcyclopentanone (V). It gave a positive iodoform reaction.

(c) *In benzene.* The methiodide of the Mannich base was insoluble in benzene so the base alone was used in this experiment. To powdered sodium (3.9 g., 0.17 atom) in benzene (150 c.c.) was added ethyl cyclopentanonecarboxylate (39 g., 0.25 mol.), and the mixture was heated gently under reflux till all the sodium had reacted. The mixture was cooled to room temperature and diethylaminobutanone (24.5 g., 0.17 mol.) in benzene (50 c.c.) added, in small quantities, over a period of 2 days. Standing for a further day produced no noticeable change, so the mixture was heated gently under reflux till all the sodio-derivative had reacted (*ca.* 1 hour). The mixture was poured into dilute hydrochloric acid, and the benzene layer separated and extracted with sodium hydrogen carbonate solution. The sodium hydrogen carbonate extract yielded, on acidification, a trace of a liquid acid. The benzene was distilled from the washed and dried solution, and the residue fractionated using a short column. The fraction (8.1 g.), b. p. 79–81°/2 mm., consisted of unreacted ethyl cyclopentanonecarboxylate. It was followed by a mixed fraction (8.2 g.), b. p. 81–139°/3 mm., and a fairly pure fraction (6.4 g.), b. p. 139°/3 mm. (Found for last fraction: C, 64.9; H, 8.0. Calc. for $C_{12}H_{18}O_4$: C, 63.7; H, 7.9%). The semicarbazone crystallised from aqueous ethanol in colourless, flattened needles, m. p. and mixed m. p. with the semicarbazone of 2-carbethoxy-2-butan-3'-onylcyclopentanone (V) 178–179° (decomp.).

Reaction of cyclopentanone with Diethylamine Hydrochloride and Paraformaldehyde in Ethanol.—A solution of cyclopentanone (34.5 g., 0.4 mol.), diethylamine hydrochloride (43 g., 0.4 mol.), and paraformaldehyde (12 g., 0.52 mol.) in ethanol (20 c.c.) was heated in a water-bath for 5 hours. At the end of this period the solution was cooled, diluted with water, basified with sodium hydroxide, and extracted with ether. The washed and dried ethereal extract yielded two fractions on distillation: fraction (i) (8 g.), b. p. 60–70°/18 mm., and fraction (ii) a viscous red oil (10 g.), b. p. 120–200°/2.5 mm. Redistillation of the first fraction gave a colourless oil, n_D^{25} 1.4665, b. p. 150–163°. The semicarbazone separated from ethanol in colourless rhombohedra, m. p. 214°, with softening and decomposition a few degrees below this temperature (Found: C, 54.9; H, 7.35. Calc. for $C_7H_{11}ON_3$: C, 54.8; H, 7.2%). Hydrogenation in methanol solution in the presence of palladium-calcium carbonate catalyst afforded a colourless oil (too small in quantity for accurate measurement of the boiling point). The semicarbazone crystallised in small colourless needles from ethanol, m. p. 167.5–168.5° (Found: C, 53.7. Calc. for $C_7H_{13}ON_3$: C, 54.2%).

* The same synthesis by Plattner, Fürst, Chopin, and Winteler (*Helv. Chim. Acta*, 1948, **31**, 501) came to our notice only after this work had been submitted for publication.

Fraction (ii) was redistilled giving a light yellow oil, b. p. 129—130°/0.1 mm., which contained no nitrogen (Found: C, 73.0, 73.4; H, 8.0, 8.0. $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.9%). This substance is considered to be *biscyclopentan-2-onylmethane* (X). The *disemicarbazone* formed minute, colourless crystals from ethanol, m. p. 227° (decomp.) (Found: C, 53.5; H, 7.6. $C_{13}H_{22}O_2N_6$ requires C, 53.0; H, 7.5%).

6-Carboethoxy-5 : 6 : 7 : 8-tetrahydroindan-5-one (XII).—The methiodide of 2-(morpholinomethyl)cyclopentanone (Harradence and Lions, *J. Proc. Roy. Soc. New South Wales*, 1939, **72**, 233) was prepared by mixing the base (9.2 g., 0.05 mol.) and methyl iodide (8.5 g., 0.06 mol.) at room temperature. The mixture warmed spontaneously after a few minutes; it was then left for about half an hour and crystallised in short colourless needles which were washed with dry ether and dried in a vacuum.

Sodium (1.44 g., 0.063 atom), dissolved in a mixture of freshly-distilled ethyl acetoacetate (8.45 g., 0.065 mol.) and absolute ethanol (50 c.c.), was treated with 2-(morpholinomethyl)cyclopentanone methiodide (16.2 g., 0.05 mol.) in absolute ethanol (100 c.c.), and the solution heated gently under reflux on a water-bath for 3 hours. The solution was then cooled, diluted with water, and ether extracted. Distillation of the dried neutral ethereal extract gave a first fraction (0.7 g.), b. p. 40—50°/0.5 mm., consisting of unchanged ethyl acetoacetate. The second fraction (4.9 g.), a yellow oil, b. p. 115—170°/1 mm., contained the desired *compound*. The fraction was redistilled, giving a pale yellow oil (2.7 g.), n_D^{25} 1.5079, b. p. 119—131°/0.5 mm. (Found: C, 69.0; H, 7.8. $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.7%). On keeping it for 2 days a crop of crystals separated from this oil. Recrystallisation from light petroleum (b. p. 30—80°) gave colourless, prismatic needles, m. p. 74—75° (Found: C, 69.1; H, 7.6%). These two substances were regarded as stereoisomers.

6-Carboethoxyhexahydroindan-5-one (XIV).—6-Carboethoxy-5 : 6 : 7 : 8-tetrahydroindan-5-one in ethanol was hydrogenated in the presence of palladium-calcium carbonate catalyst [2% Pd, prepared according to Busch and Stöve (*Ber.*, 1916, **48**, 1063)] at 4 atmospheres, the theoretical amount of hydrogen being absorbed in 4 hours. The *hexahydroindanone* distilled as a colourless oil, n_D^{25} 1.4960, b. p. 113—118°/0.05 mm. (Found: C, 68.8; H, 8.5. $C_{12}H_{16}O_3$ requires C, 68.6; H, 8.6%).

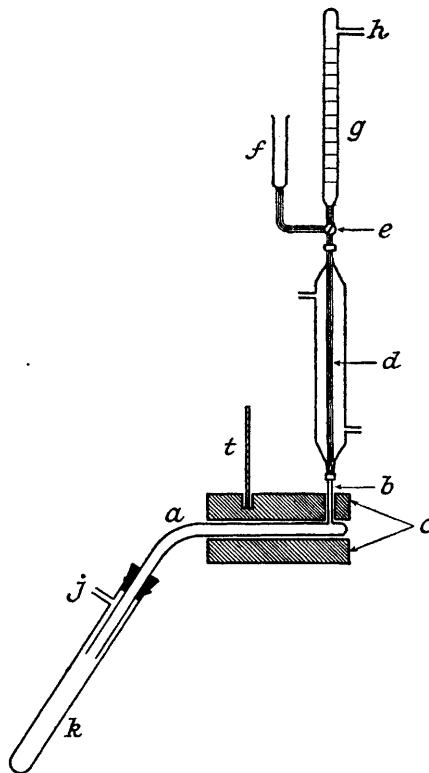
Hexahydroindan-5-one (XV).—The above keto-ester (7.9 g.) was heated with glycerol (100 c.c.) and water (10 c.c.) at 180—190° for 4 hours. After dilution of the mixture with two volumes of water the product was isolated by ether extraction. Distillation of the dried neutral extract yielded a colourless oil (2.5 g.), b. p. 65—95°/1 mm. For analysis this was redistilled, n_D^{27} 1.4814, b. p. 110—114°/17 mm. (Found: C, 77.3; H, 9.9. Calc. for $C_9H_{14}O$: C, 78.2; H, 10.1%). The *semicarbazone* separated from ethanol or dilute acetic acid in colourless, feathery needles, m. p. 193—195.5° (decomp.) when heated at the rate of 1°/min., and m. p. 183—186° when heated at the rate of 0.5°/min. (Found: C, 61.9; H, 8.4. Calc. for $C_{10}H_{17}ON_3$: C, 61.5; H, 8.7%). Plattner, Fürst, and Studer (*loc. cit.*) give m. p. 187° for a stereoisomeric mixture of hexahydroindan-5-ones. Cook and Linstead (*J.*, 1934, 946) give m. p. 203° for the *cis*-isomer whilst Hüchel and Goth (*Ber.*, 1934, **67**, 2104) give m. p. 208° for the same isomer.

bicyclo[5 : 3 : 0]Decan-3-one (XVI).—Hexahydroindan-5-one (2 g., 0.015 mol.) in a little absolute ether at 0° was treated with diazomethane (0.82 g., 0.02 mol.) in absolute ether (50 c.c.). Absolute methanol (15 c.c.) was then added. No evolution of nitrogen took place till the solution warmed to room temperature. After 24 hours the colour of the solution had noticeably decreased, and after 3 days hardly any colour remained. The ether and most of the methanol were removed under reduced pressure, and the semicarbazone formed from the residue. The semicarbazone (1.65 g.) crystallised in thick, short needles from ethanol, and after 6 recrystallisations had m. p. 158.5—159.5° (Found: C, 63.2; H, 9.1. Calc. for $C_{11}H_{19}ON_3$: C, 63.2; H, 9.1%). The mother liquors yielded on concentration another semicarbazone crystallising in small colourless needles, m. p. 145—149°, from ethanol (Found: C, 63.4; H, 9.1%). These derivatives are regarded as stereoisomers. The mixed semicarbazones (1 g.) were hydrolysed with 10% hydrochloric acid (20 c.c.) and the regenerated ketone taken up in ether. Distillation of the dried, neutral extract yielded 0.75 g., b. p. 118—122°/12 mm.

bicyclo[5 : 3 : 0]Decan-3-ol (XVII).—Sodium (1.5 g.) was added to the *bicyclo[5 : 3 : 0]decan-3-one* in absolute ethanol (20 c.c.), in small quantities, over a period of 5 minutes. The mixture was shaken occasionally until all the sodium had dissolved, after which water was added. The *bicyclo[5 : 3 : 0]decan-3-ol* was extracted with ether. Distillation of the dried neutral extract afforded a colourless viscous oil (2.47 g.), $n_D^{15.5}$ 1.4980, b. p. 120—127°/11—12 mm. (Found: C, 77.4; H, 11.8. $C_{10}H_{18}O$ requires C, 77.9; H, 11.7%).

Dehydrogenation of bicyclo[5 : 3 : 0]Decan-3-ol.—The dehydrogenation apparatus is shown diagram-

FIG. 3.
Dehydrogenation apparatus.



* We are indebted to Mr. D. H. S. Horn for the design of the apparatus used in this experiment.

matically in Fig. 3. The catalyst chamber (*a*) was constructed from "Pyrex" glass of about 12 mm. internal diameter and provided with an inlet tube (*b*) of about 1 mm. internal diameter. The heating block (*c*) (shown in section in the diagram) consisted of two superposed copper blocks, each of which had a semicircular channel, which together formed a cylindrical channel to accommodate the catalyst chamber (*a*). In addition the top block had two circular holes which accommodated the inlet tube (*b*) and the thermometer (*t*). It had a length of 5 in. and a cross-section of 2 in. by 2 in. This large size made it possible to control the temperature to well within 5° at over 300°, when using an ordinary gas burner as the source of heat. A very fine capillary tube (*d*) 20 cm. long and about 0.15 mm. internal diameter, was attached to the tube (*b*) by means of pressure tubing. The tube (*d*) was surrounded by a water-jacket to keep the temperature of the liquid flowing through it constant. This precaution ensured that the liquid in the capillary tube was maintained at a constant viscosity which greatly facilitated the attainment of a steady flow. The top of the capillary tube was attached, by means of rubber tubing, to one arm of a three-way tap (*e*). One of the other arms was fused to a reservoir (*f*) and the remaining arm to a 2 c.c. graduated pipette (*g*). The top of the pipette was sealed off, and near the top a side arm (*h*) was attached. The tube (*h*) was connected, by means of pressure tubing, to a 50 c.c. gas burette, containing mercury. The side arm (*j*) of the receiver (*k*) was connected to a water pump, which maintained a constant vacuum in (*a*). Since the pressure in (*a*) was constant, the rate of flow of liquid through (*d*) could be controlled by adjusting the pressure on the liquid in (*g*). This was done by raising or lowering the level of the mercury in the gas burette. The catalyst chamber (*a*) was packed with a mixture of 30% palladium-charcoal catalyst (Linstead and Thomas, *J.*, 1940, 1130) and freshly-ignited long fibre asbestos (1 : 1 by weight). The liquid to be dehydrogenated was placed in (*f*). The catalyst chamber was evacuated, gradually at first so as not to displace the catalyst, and the heating block raised to the desired temperature. The pipette (*g*) was filled through the tap (*e*) and the liquid then allowed to flow down the capillary tube into the chamber (*a*) where it was vapourised. The optimum rate of flow for most dehydrogenations carried out was found to be about 0.01 c.c./min. Proceeding in this way *bicyclo*[5 : 3 : 0]decan-3-ol (0.5 g.) was dehydrogenated at 350°. The intensely blue product was distilled in a vacuum, the pale blue fraction, boiling up to 100°/16 mm., being rejected. The very intensely blue residue (0.2 g.) was warmed in ethanol (0.5 c.c.) with 2 : 4 : 6-trinitrotoluene (0.03 g.). The black-brown needles of the complex which separated on cooling were recrystallised from ethanol. Repeated recrystallisation did not raise the m. p. above 94–95°. Plattner and St. Pfau (*Helv. Chim. Acta*, 1937, 20, 224) give m. p. 99.5–100° (corr.) for the trinitrotoluene complex with azulene. The amount of material at this stage was so small that an analysis was not possible.

9 : 10-Benzobicyclo[5 : 3 : 0]dec-9-en-3-one (XIX).—Hexahydrofluoren-3-one (3 g., 0.016 mol.) prepared according to the directions of Harradence and Lions (*loc. cit.*) in absolute ether (10 c.c.) was added to an ice-cold ethereal solution (34.5 c.c.) of diazomethane (containing 0.88 g., 0.021 mol., of diazomethane), which had previously been dried over sodium for 3 hours. When methanol (16.5 c.c.) was added there was an immediate evolution of nitrogen. After 2 hours at 0° the solution was allowed to warm up to room temperature (15–16°). The ether and methanol were removed in a vacuum after 3 days and the residue, in a little ethanol, was treated with excess of semicarbazide hydrochloride and potassium acetate. The semicarbazone, which would not crystallise, was washed by decantation with water and a little alcohol. It was then hydrolysed with 10% hydrochloric acid (30 c.c.) and the resulting ketone taken up in ether. Distillation of the dried neutral extract afforded a main fraction (1.70 g.), b. p. 138–154°/0.5 mm. Redistillation gave a viscous oil, b. p. 130–134°/0.1 mm. Both the oxime and the semicarbazone failed to crystallise. The 2 : 4-dinitrophenylhydrazone separated from ethanol in flattened, yellow needles, m. p. 194–195° (Found: C, 62.8; H, 5.5. $C_{20}H_{20}O_4N_4$ requires C, 63.2; H, 5.2%). The 2 : 4-dinitrophenylhydrazone of this ketone from another experiment had m. p. 162–164°. Both of these derivatives depressed the m. p. of hexahydrofluoren-3-one 2 : 4-dinitrophenylhydrazone.

9 : 10-Benzobicyclo[5 : 3 : 0]dec-9-en-3-ol (XX).—Sodium (0.5 g.) was added in small quantities to a solution of 9 : 10-benzobicyclo[5 : 3 : 0]dec-9-en-3-one (1.09 g.) in absolute ethanol (9 c.c.). When all the sodium had dissolved the solution was diluted with water, and the product isolated with ether. Distillation of the dried, neutral extract afforded the alcohol as a very viscous, practically colourless oil (0.71 g.), n_D^{25} 1.5628, b. p. 125–130°/0.5 mm. (Found: C, 83.5; H, 8.4. $C_{14}H_{18}O$ requires C, 83.2; H, 8.9%).

1 : 2-Benzazulene (XXI).—Dehydrogenation of 9 : 10-benzobicyclo[5 : 3 : 0]dec-9-en-3-ol (3.3 g.) was successfully accomplished using the apparatus and procedure previously described. The optimum temperature was 330° and the optimum rate of flow 0.01 c.c./min. The first few drops of distillate from the dehydrogenation solidified to a colourless crystalline substance, m. p. 94–97°. This may have been phenanthrene (m. p. 99°) formed by intramolecular rearrangement of 1 : 2-benzazulene. This colourless distillate was followed by an intensely blue, almost black distillate. The latter was taken up in light petroleum (b. p. 20–40°), and cooled in ice. The benzazulene was extracted from this solution by shaking with ice-cold 85% phosphoric acid (70 c.c.) in three separate portions. The phosphoric acid solution, deep yellow in colour, was shaken several times with ice-cold petroleum to remove any unchanged material. In order to liberate the benzazulene, this solution was poured slowly into a mixture of crushed ice (800 g.) and peroxide-free ether (1000 c.c.). Evaporation of the solvent from the dried, neutral ethereal solution afforded crude crystalline 1 : 2-benzazulene (1.01 g.). The combined petroleum extracts from the above were washed, dried, and the solvent evaporated, leaving a mobile oil (2.2 g.). This was recycled through the dehydrogenation apparatus to yield a further 0.3 g. of crude 1 : 2-benzazulene. The 1 : 3 : 5-trinitrobenzene derivative was formed by warming a mixture of 1 : 2-benzazulene (14 mg.), trinitrobenzene (16 mg.), and ethanol (3 c.c.) till solution occurred. On cooling, the complex separated as long black-brown needles which only required one recrystallisation, m. p. 152.5–153.5° (Found: C, 61.6; H, 3.6. $C_{20}H_{13}O_6N_3$ requires C, 61.4; H, 3.35%). The complex with 2 : 4 : 6-trinitrotoluene was formed in an analogous manner. It separated from ethanol in stout, flattened, dark brown needles, m. p. 105.5–106.5° (Found: C, 62.6; H, 4.1. $C_{21}H_{15}O_6N_3$ requires C, 62.2; H, 3.7%). The pure hydrocarbon was obtained by allowing the 2 : 4 : 6-trinitrotoluene derivative (200 mg.), in a 1 : 1 mixture (20 c.c.) of benzene and cyclohexane, to flow down a column of

alumina (B.D.H. "Chromatographic Grade") 14 cm. in height and 1.4 cm. in diameter. The *benzazulene* was eluted from the column with pure *cyclohexane* leaving the trinitrobenzene behind. Evaporation of the solvent and recrystallisation of the residue from ethanol gave deep green plates, m. p. 176—177° (decomp.) (Found: C, 94.7; H, 6.1. $C_{14}H_{10}$ requires C, 94.4; H, 5.6%).

The Action of Diazoacetic Ester on Fluorene.—Diazoacetic ester (7.5 g.) was added dropwise over a period of 5 hours to vigorously stirred fluorene (70 g.), kept at 130°. After cooling, the mixture was dissolved in the minimum of boiling ethanol to which was added potassium hydroxide (20 g.) in a little water. After heating under reflux for 2 hours, the solution was cooled, and the excess of fluorene filtered off. Most of the ethanol was distilled off, water was added, and the mixture was thoroughly extracted with ether to remove any fluorene. The aqueous solution was then acidified, and the acid collected in ether. Evaporation of the ether from the dried extract left a viscous green acid (6.6 g.) which contained a certain amount of nitrogenous polymerisation products of diazoacetic ester. This acid (2.3 g.) was mixed with palladium-charcoal (0.2 g.), and distilled (free flame) in a vacuum (15 mm.). The solid green distillate was taken up in light petroleum (b. p. 20—40°), and shaken with alkali to remove any acid. This solution was then dried, and the 1:2-benzazulene extracted with 85% phosphoric acid as previously described, giving 0.6 g. of crude 1:2-benzazulene. The 1:3:5-trinitrobenzene derivative had m. p. and mixed m. p. (with the product from the last synthesis) 150—153° (Found: C, 61.6; H, 3.6%).

Absorption Spectra.—The measurements of the absorption spectrum of 1:2-benzazulene were carried out in *cyclohexane* solution using a Beckman Quartz spectrophotometer.

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