109. *Azulenes. Part I. Synthesis of Vetivazulene.*

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Condensation of ethyl 4-*iso*propyl*cyclo*pentanone-2-carboxylate (II) with Δ^{β}-hexen-δ-one (III) by the Michael–Claisen–Robinson reaction gave a keto-ester (IV), which was converted by decarbethoxylation and then reduction into a mixture of dicyclic ketones represented by the structure (V). A pure constituent of this mixture was isolated, and its structure established. Vetivazulene (VIII) has been synthesised from the mixture (V) by ring-enlargement with diazomethane, followed by dehydrogenation with selenium.

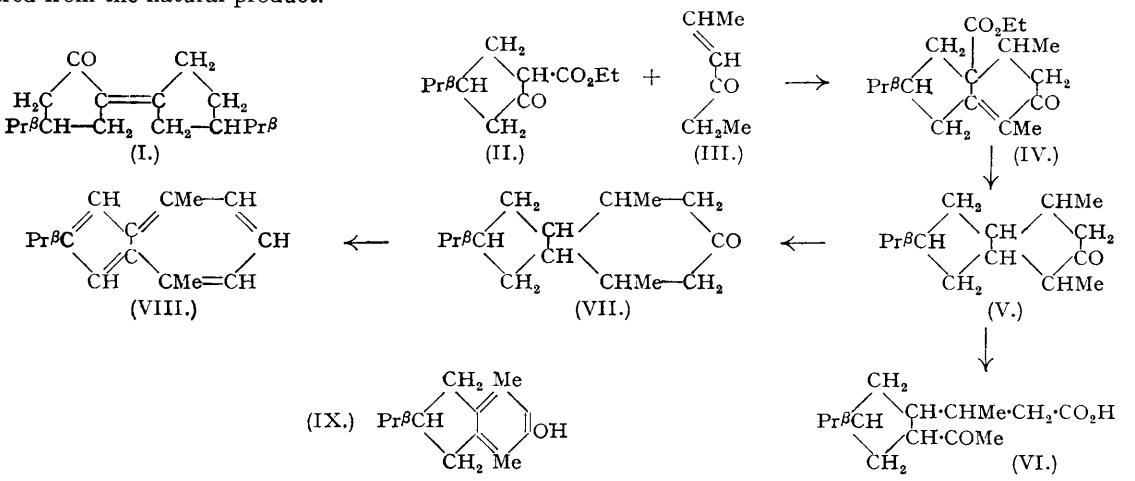
The elucidation by St. Pfau and Plattner (*Helv. Chim. Acta*, 1936, **19**, 858; 1937, **20**, 224, 469) of the type of structure present in the blue hydrocarbons obtained by dehydrogenation of certain essential oils made it of interest to study the synthesis and chemical properties of members of this group of coloured hydrocarbons. Interest in these compounds was reinforced by the elegant analytical proof, published while the present work was in progress (St. Pfau and Plattner, *ibid.*, 1940, **23**, 768), that the dicyclic hydroazulene system is in fact present in β-vetivone, a constituent of vetiver oil (*idem, ibid.*, 1939, **22**, 640; compare Sabetay and Traband, *Bull. Soc. chim.*, 1942, **8**, 152).

It was decided in the first instance to undertake the synthesis of vetivazulene (VIII), a product of dehydrogenation of Java vetiver-oil. Our synthesis was well under way when it found that vetivazulene had already been synthesised by another method (*idem, ibid.*, 1939, **22**, 202), which, however, did not completely establish the structure. This prior work made it possible to devote less attention to the rather troublesome later stages of our synthesis than would otherwise have been necessary.

The type of method which we adopted was that developed with such success by Robinson and his collaborators (*e.g.*, Rapson and Robinson, J., 1935, 1285; du Feu, McQuillin, and Robinson, J., 1937, 53) for the synthesis of polycyclic ketones. Attempted condensation of sodio-3-*iso*propyl*cyclo*pentanone with Δ^{β}-hexen-δ-one (III) gave unsatisfactory results on account of the large proportion of 3-*iso*propyl*cyclo*pentanone converted into di*iso*propyl*cyclo*pentylidene*cyclo*pentanone (probably I) by sodamide in cold ether. Δ^{β}-Hexen-δ-one (III) condensed smoothly, however, with the sodio-derivative of ethyl 4-*iso*propyl*cyclo*pentanone-2-carboxylate (II). The resulting mixture of esters (IV) underwent successive hydrolysis and decarboxylation with boiling alcoholic potash. The ready hydrolysis of the quaternary ester and the lability of the resulting acid are unusual and must be ascribed to stereochemical influences. Hydrogenation with palladium of the unsaturated ketones so formed gave a mixture of stereoisomeric ketones (V), from which one pure component was isolated through its *semicarbazone*. Oxidation of the mixed ketones with chromic acid gave not only the β-(2-*acetyl*-4-iso*propyl*-cyclo*pentyl*)*butyric acid* (VI) formed by similar treatment of the stereochemically pure *ketone* (V), but also a stereoisomeric *keto-acid* (VI).

The m. p. of the semicarbazone of the pure ketone (V) is not very different from that of the semicarbazone

of the dimethyl*iso*propylhydrindanone obtained by St. Pfau and Plattner (*Helv. Chim. Acta*, 1940, **23**, 768) by degradation of tetrahydro-β-vetivone (VII) and it is possible that our synthetic ketone is identical with that prepared from the natural product.



It was expected that the action of diazomethane on the ketone (V) would lead to enlargement of the six-membered ring to a seven-membered ring with formation of optically inactive tetrahydrovetivone (VII) (compare Mosettig and Burger, *J. Amer. Chem. Soc.*, 1930, **52**, 3456; Adamson and Kenner, J., 1939, 181). However, the only pure compound isolated from this reaction was a ketone which was shown by analysis of its *semicarbazone* to be an isomeride rather than a homologue of (V). The isomerisation doubtless involves an inversion of configuration about the asymmetric carbon atom adjacent to the carbonyl group. Nevertheless, selenium dehydrogenation of the crude product of the action of diazomethane on the mixed ketones (V) gave in addition to 4 : 7-dimethyl-2-*iso*propyl-5-indanol (IX) a small yield of vetivazulene (VIII). The latter, which has a characteristic purple colour, was isolated as its complex with *s*-trinitrobenzene. A trimethylazulene, believed to have the substituents in the same positions as in vetivazulene, has recently been described (Schechter and Haller, *J. Amer. Chem. Soc.*, 1941, **63**, 3507).

In view of the interest attached to the synthesis of tetrahydrovetivone (VII) it is proposed to explore other possible methods for obtaining it from (V) or (VI).

Experimental.

All m. p.'s are corrected.

Ethyl 4-iso*Propyl*cyclo*pentanone-2-carboxylate* (II).—Benzene was converted successively into cumene, potassium *p*-cumenesulphonate *p-iso*propylphenol, *p-iso*propyl*cyclo*hexanol, β-*iso*propyladipic acid, and ethyl 4-*iso*propyl*cyclo*pentanone-2-carboxylate. The sulphonation and the alkaline fusion proved very laborious when carried out on the necessary scale with laboratory apparatus. Cumene was prepared by the procedure of Meyer and Bernhauer (*Monatsh.*, 1929, **53** and **54**, 721), which proved somewhat more economical than the method of Haworth and Barker (J., 1939, 1302). After sulphonation (Gerhardt and Cahours, *Annalen*, 1841, **38**, 92; Spica, *Gazzetta*, 1879, **9**, 433) the *p*-sulphonic acid was isolated as its barium salt.

A mixture of fuming sulphuric acid (600 g.; 12% of sulphur trioxide) and concentrated sulphuric acid (400 g.) was slowly added with shaking to cumene (500 g.) below 40°. When homogeneous (1 hour), the mixture was kept for 3 hours and poured into water (4 l.), a smooth paste of calcium hydroxide (760 g.) (preferable to barium carbonate) added, and the liquid filtered. The solid was extracted with boiling water (3 l.), and the combined filtrates evaporated to 2 l. and filtered from a small sediment. A slight excess of barium chloride was added, and the barium salt collected and dried. A solution of the barium salt (500 g.) in boiling water (6 l.) was treated with potassium carbonate until just alkaline to phenolphthalein; after filtration the solution was evaporated to dryness. When the potassium salt was fused with potash at 280—300°, it gave *p-iso*propylphenol (b. p. 217—222°, m. p. 62—63°) in 50—55% yield (Paternò and Spica, *Gazzetta*, 1876, **6**, 535).

Hydrogenation of *p-iso*propylphenol over platinum-black is stated (Vavon and Callier, *Bull. Soc. chim.*, 1927, **41**, 677) to give a mixture of stereoisomeric 4-*iso*propyl*cyclo*hexanols (66%) and 4-*iso*propyl*cyclo*hexane (33%). By the use of a Raney nickel catalyst at 180° 4-*iso*propyl*cyclo*hexanol was readily obtained in 80% yield. The catalyst was prepared by addition of 50% aluminium–nickel alloy (16 g.; 100 mesh) to a stirred solution of potassium hydroxide (16 g.) in water (300 c.c.). When the initial reaction had subsided, the temperature was raised slowly to 100° and maintained until the reaction had almost ceased (2 hours.). The alkaline solution was decanted, and the catalyst washed by decantation, six times with hot water and once with alcohol. A mixture of *p-iso*propylphenol (200 g.) and this catalyst (8 g.) was introduced together with hydrogen into a high-pressure autoclave,* the pressure of hydrogen being 100 atms. at 180°. Stirring was effected with a stainless steel stirrer, the gland being lubricated with glycerol. The pressure fell rapidly to 30 atms., and was raised by the inlet of more hydrogen. When the theoretical amount had been absorbed (3 hours), the pressure remained constant and the resulting 4-*iso*propyl*cyclo*hexanol was distilled (b. p. 102—110°/15 mm.).

Oxidation of this carbinol to β-*iso*propyladipic acid with alkaline permanganate (v. Braun and Werner, *Ber.*, 1929, **62**, 1054) gave the required acid, but a better yield was obtained with 50% nitric acid catalysed by ammonium vanadate. This salt (0·2 g.) was dissolved in a mixture of concentrated nitric acid (250 c.c.) and water (125 c.c.) at 50—60°. 4-*iso*-

* We are much indebted to Professor W. M. Cumming for facilities, including the use of an autoclave, afforded at the Royal Technical College for this hydrogenation.

Propyl*cyclo*hexanol (100 g.) was added to the vigorously stirred solution at such a rate that the temperature was maintained at 50—55° without external heat (4—5 hours). The temperature was then raised to 100° for ½ hour, and the excess of water and nitric acid removed at 100° under reduced pressure. The residual β-*iso*propyladipic acid was esterified with ethyl alcohol and hydrogen chloride, and the ester distilled (135 g.; b. p. 145—165°/15 mm.).

For the Dieckmann reaction, sodium (15 g.) was atomised in dry toluene (200 c.c.), and ethyl β-*iso*propyladipate added at such a rate that the reaction could be controlled readily. The mixture was refluxed for 80 minutes (oil-bath at 120—130°), with occasional shaking, and cooled to 0°, ice-cold 10% hydrochloric acid (1 l.) added, and the whole shaken until no more solid remained. The separated toluene solution was washed with sodium carbonate solution and water, dried, and distilled. The resulting ethyl 4-*iso*propyl*cyclo*pentanone-2-carboxylate (64 g.; 65% yield) had b. p. 128—135°/15 mm., and gave an intense purple colour with alcoholic ferric chloride.

Hydrolysis of this ester (14 g.) by 4½ hours' boiling with 3N-hydrochloric acid (140 c.c.), followed by steam distillation, gave 3-*iso*propyl*cyclo*pentanone (8·5 g.), b. p. 75—80°/15 mm. Its semicarbazone had m. p. 192° (cf. Bouveault and Blanc, *Compt. rend.*, 1908, **146**, 233; **147**, 1314; Wallach, *Annalen*, 1912, **388**, 59) and its phenylhydrazone formed colourless plates, m. p. 75—76·5°.

Δ^{β}-*Hexen*-δ-*one* (III).—Oxidation of the carbinol resulting from the interaction of ethylmagnesium bromide and crotonaldehyde could not be effected by Oppenauer's method, aluminium *iso*propoxide, acetone, and benzene being used, or by chromic acid (after protection of the double bond by addition of bromine), and chromic acid oxidation of the corresponding δ-chloro-Δ^{β}-hexene (cf. Courtot and Pierron, *Bull. Soc. chim.*, 1929, **45**, 290) gave the required ketone in very poor yield. Recourse was therefore had to Blaise's method (*ibid.*, 1905, **33**, 39, 45), whereby allylzinc halide was condensed with propionitrile, and the ethyl allyl ketone isomerised by boiling dilute sulphuric acid. An attempt to improve this method by substituting allylmagnesium bromide (cf. Gilman and McGlumphy, *ibid.*, 1928, **43**, 1322) was unsuccessful. Allyl bromide was used in place of the allyl iodide used by Blaise (*loc. cit.*).

Interaction of Sodio-3-iso*propyl*cyclo*pentanone with* Δ^{β}-*Hexen*-δ-*one*.—A slow current of nitrogen was passed for 4 hours through a stirred suspension of powdered sodamide (3·2 g.) in 3-*iso*propyl*cyclo*pentanone (18 g.) and dry ether (60 c.c.), Δ^{β}-hexen-δ-one (8 g.) added slowly, stirring continued at room temperature for 4 hours, the mixture refluxed for 6 hours, and the product decomposed with hydrochloric acid. An ethereal extract was evaporated, unchanged ketones removed in steam, and the residue distilled at 10 mm., giving fractions (1) 7 g., b. p. 150—170°, (2) 5·1 g., b. p. 170—190°, and (3) 4 g., b. p. 190—220°. Fraction (2) gave a solid which crystallised from aqueous alcohol in white plates, m. p. 75—76°. This was evidently not a condensation product but was formed by the action of sodamide on 3-*iso*propyl*cyclo*pentanone, for the same ketone (probably I) (5 g.) was isolated when the cyclic ketone (14 g.) was stirred for an hour at − 20° with sodamide (3·9 g.) in ether (50 c.c.). This unsaturated ketone was hydrogenated over palladium-black in acetone to a saturated ketone which gave a *semicarbazone*, m. p. 161·5° (from acetone) (Found: C, 69·8; H, 10·85. $C_{19}H_{31}ON_3$ requires C, 69·6; H, 10·7%), and an oxime, m. p. 142—143·5° (from alcohol) (Found: C, 76·3; H, 11·7. Calc. for $C_{18}H_{29}ON$: C, 76·5; H, 11·65%). Wallach and Worlitzer (*Nachr. K. Ges. Wiss. Göttingen*, 1915, **1**, 17) obtained the bimolecular condensation product of 3-*iso*propyl*cyclo*pentanone by treatment with cold sodium ethoxide. They gave the m. p. as 77—78°, and obtained by hydrogenation a saturated ketone of which the oxime had m. p. 136°.

Condensation of Ethyl 4-iso*Propyl*cyclo*pentanone*-2-*carboxylate* (II) *with* Δ^{β}-*Hexen*-δ-*one* (III).—To the thick paste of sodio-compound obtained by adding the keto-ester (130 g.) to a solution of sodium ethoxide (12 g. of sodium in 650 c.c. of absolute alcohol distilled over quicklime) was added a solution of Δ^{β}-hexen-δ-one (50 g.) in absolute alcohol (200 c.c.). The whole was kept at room temperature for 60 hours (most of the solid had dissolved after 12 hours), the solution then heated, much of the alcohol (650 c.c.) distilled, and the residual solution poured into ice and water and extracted with ether. The aqueous alkaline solution was acidified, and the precipitated oil separated into fractions soluble in sodium carbonate (this was essentially *iso*propyladipic acid and gave 12 g. of ethyl ester when esterified) and in sodium hydroxide (this fraction gave an intense purple colour with ferric chloride and was apparently unchanged keto-ester). The ethereal extract of neutral product, which gave no colour with alcoholic ferric chloride, was distilled at 12 mm. into fractions (i) 14 g., b. p. 120—170°, and (ii) 70 g., b. p. 170—190°.

Fraction (ii), consisting of the dicyclic keto-ester (IV), was hydrolysed by 6 hours' boiling with alcohol (400 c.c.) and potassium hydroxide (50 g. in 35 c.c. of water), potassium carbonate separating. Some of the alcohol was distilled off, and the solution diluted with water and extracted with ether. The alkaline solution gave very little product on acidification. The ethereal extract was distilled and gave a yellowish liquid (43 g.), b. p. 160—170°/14 mm. This was essentially the unsaturated ketone formed by decarbethoxylation of (IV), but it yielded no crystalline derivatives.

Hydrogenation of this material, dissolved in alcohol (250 c.c.), over palladium-black (0·5 g.) was complete in 25 hours (hydrogen absorption, 4·2 l.). Treatment of an aqueous-alcoholic solution of the resulting saturated ketones (V) with semicarbazide, followed by crystallisation from alcohol, gave 7·2 g. of pure *semicarbazone*, which formed colourless leaflets, m. p. 204—205° (Found: C, 68·4; H, 10·2; N, 15·7. $C_{15}H_{27}ON_3$ requires C, 68·0; H, 10·3; N, 15·85%). The *oxime*, prepared from another portion of the mixed saturated ketones by heating with hydroxylamine hydrochloride in pyridine, formed fine white needles, m. p. 154·5° (Found: C, 75·1; H, 10·9. $C_{14}H_{25}ON$ requires C, 75·3; H, 11·3%).

The liquor from which the pure semicarbazone had been isolated gave only resinous material on dilution with water. This consisted of a semicarbazone mixture, from which the ketones were regenerated by steam-distillation with 20% sulphuric acid. The resulting ketone mixture was used in some experiments described below. The poor yield of pure semicarbazone hindered the subsequent stages of the synthesis, and the yield was not improved in other experiments in which the conditions of interaction of (II) and (III) were somewhat modified.

Stereochemically Pure 4 : 7-*Dimethyl*-2-iso*propyl*-5-*hydrindanone* (V).—The pure semicarbazone, m. p. 204°, was hydrolysed by steam-distillation with 20% sulphuric acid (200 c.c.). The regenerated ketone was extracted from the steam-distillate with ether, and the extract dried (sodium sulphate) and evaporated on the water-bath. The pure *ketone*, distilled at 0·3 mm. from an air-bath at 100°, formed a colourless liquid with a feeble peppermint odour, and had $d_4^{16°}$ 0·9419 and $n_D^{16°}$ 1·4778; whence $[R_L]_D$ = 62·52 (calc., 62·70) (Found: C, 80·4; H, 11·7. $C_{14}H_{24}O$ requires C, 80·7; H, 11·6%). Reconversion of this ketone into the same semicarbazone from which it was prepared showed that the sulphuric acid used for hydrolysis did not effect configurational change. A crystalline benzylidene derivative was not obtained from this ketone.

Dehydrogenation of the pure ketone (1 g.) with palladium-black (0·1 g.) was effected by heating for 9 hours at 290—300° in an evacuated sealed tube. The resulting 4 : 7-dimethyl-2-*iso*propyl-5-indanol (IX) (0·25 g.), isolated by digestion with light petroleum, in which it was sparingly soluble, crystallised from hexane in colourless needles, m. p. 133—134° (Found: C, 81·9; H, 9·5. Calc. for $C_{14}H_{20}O$: C, 82·3; H, 9·9%) (St. Pfau and Plattner, *Helv. Chim. Acta*, 1940, **23**, 792, give m. p. 129—130°). This dehydrogenation product had the character of a cryptophenol (cf. Farinholt, Harden, and Twiss, *J. Amer. Chem. Soc.*, 1933, **55**, 3383). It gave a 3 : 5-*dinitrobenzoate*, which crystallised from alcohol in fine, colourless needles, m. p. 145—146° (Found: C, 63·6; H, 5·8; N, 7·4. $C_{21}H_{22}O_6N_2$ requires C, 63·3; H, 5·6; N, 7·0%).

β-(2-*Acetyl*-4-iso*propyl*cyclo*pentyl*)*butyric Acid* (VI).—A solution of the pure ketone (V) (0·5 g.) in glacial acetic acid was treated with a concentrated aqueous solution of chromic acid (0·2 g.). The solution was warmed to 75° and then allowed to cool slowly. The acidic oxidation product gave a *semicarbazone* ((0·15 g.) which crystallised from alcohol in

short colourless needles, m. p. 181—182° (Found: C, 60·9; H, 9·2; N, 14·3. $C_{15}H_{27}O_3N_3$ requires C, 60·5; H, 9·1; N, 14·1%).

Hydrolysis of this semicarbazone (1·5 g.) by aqueous sulphuric acid in boiling alcohol, followed by alkaline hydrolysis of the ester, gave colourless slender needles, m. p. 64—65° (from hexane), consisting of *β-(2-acetyl-4-isopropylcyclopentyl)-butyric acid* (VI) (Found: C, 69·9; H, 10·2. $C_{14}H_{24}O_3$ requires C, 69·9; H, 10·1%). Its p-*phenylphenacyl* ester formed colourless leaflets (from alcohol), m. p. 75—76° (Found: C, 77·8; H, 7·9. $C_{28}H_{34}O_4$ requires C, 77·8; H, 7·7%).

Examination of Crude Mixture of Stereoisomeric Dicyclic Ketones (V).—The material recovered by steam-distillation with 20% sulphuric acid of the mixture present in liquors from which the semicarbazone, m. p. 204°, had been isolated (see above) was treated with chromic acid with the object of oxidising any hydroxylic compounds present. For this purpose a solution of chromic acid (20 g.) in 80% acetic acid (50 c.c.) was added to a solution of the oil in glacial acetic acid (250 c.c.). The temperature rose slowly to 45°. After being kept overnight, the solution was poured into water and extracted with ether. By shaking the extract with sodium carbonate solution there was removed some acidic oxidation product, isolated as a yellow gum (8 g.). This gave a solid mixture of semicarbazones (6 g.), which was separated by fractional crystallisation from alcohol into the semicarbazone (2·6 g.), m. p. 181°, of the substituted butyric acid (VI) already described, and a more soluble *semicarbazone*, m. p. 151—155°, of an isomeric keto-acid. This crystallised from alcohol in colourless leaflets (2 g.) (Found: C, 60·8; H, 9·2%) and was hydrolysed to a keto-acid which formed a gum. This gave a p-*phenylphenacyl* ester, which crystallised from methyl alcohol in colourless microscopic leaflets, m. p. 66—67° (Found: C, 77·3; H, 7·9%). The m. p. was slightly but definitely depressed by the stereoisomeric ester, m. p. 75°. As one of the three substituents in the *cyclo*pentane ring is an acetyl group, it is unlikely that there would be more than two optically inactive stable forms of the keto-acid (VI). In the case of the dicyclic ketone (V) the number of possible stereoisomerides is considerable.

The neutral fraction recovered from this oxidation experiment formed a yellow oil (25 g.), b. p. 145—155°/12 mm. Crystalline semicarbazones could not be obtained from it, and it was resistant to hydrogenation over platinum-black. This material was used for subsequent stages of the synthesis.

Action of Diazomethane on 4 : 7-*Dimethyl*-2-iso*propyl*-5-*hydrindanone* (V).—(i) In view of the finding of Adamson and Kenner (*loc. cit.*) that ethereal diazomethane reacts exceedingly slowly with 2-methyl*cyclo*hexanone we adopted in the first instance the experimental conditions which enabled these workers to obtain 2- and 3-methyl*cyclo*heptanone. Anhydrous potassium carbonate (0·1 g.) was added to a solution of the pure dicyclic ketone (V) (2 g.) in absolute alcohol (2 c.c.). Nitrosomethylurethane (1·4 g.) was added during 3 days, the mixture being kept at 0°. After 2 further days the alcohol was removed from the filtered solution. The resulting oil, which, like the original ketone, did not react with sodium bisulphite, was treated with semicarbazide hydrochloride and sodium acetate in cold aqueous alcoholic solution. The resulting crystalline product was not homogeneous, but by crystallisation from alcohol there was readily isolated a *semicarbazone* in well-formed colourless needles, m. p. 167—168° (Found: C, 67·9, 68·1, 68·7; H, 10·1, 10·2, 10·15; N, 15·6, 15·9. $C_{15}H_{27}ON_3$ requires C, 68·0; H, 10·3; N, 15·85%. $C_{16}H_{29}ON_3$ requires C, 68·8; H, 10·5; N, 15·0%). These analyses, carried out on two different specimens of the semicarbazone, suffice to show that isomerisation rather than ring-enlargement had taken place.

(ii) Methyl alcohol (9 c.c.) was added to a solution of the pure ketone (V) (2 g.) in ethereal diazomethane (from 3 c.c. of nitrosomethylurethane, 35 c.c. of ether, and 3·6 c.c. of 25% methyl-alcoholic potassium hydroxide). Slow liberation of nitrogen set in and after 48 hours this had almost ceased and the solution was nearly colourless. The oil remaining after removal of the solvents gave a semicarbazone (2·7 g.), m. p. 145—150°. A pure component could not be obtained from this by fractional crystallisation. An unsuccessful attempt was made to obtain a crystalline dibenzylidene derivative from the ketone mixture formed from this by hydrolysis with 20% sulphuric acid (tetrahydro-β-vetivone gives such a derivative).

(iii) The neutral oil recovered from the oxidation of the mixture of ketones (V) (20 g.) was treated with diazomethane for 5 days at room temperature, as described under (ii). Ketonic material (11 g.) was separated from the product by means of Girard's reagent T. Treatment of some of this (5 g.) with semicarbazide gave a resinous mixture of semicarbazones, an alcoholic solution of which deposited crystals (0·5 g.) on long standing. These consisted of the semicarbazone, m. p. 167—168°, described under (i).

Vetivazulene (VIII).—Although tetrahydro-β-vetivone (VII) or a stereoisomeride was not isolated from the foregoing experiments with diazomethane, the presence in the mixed products of a compound of this structure was shown by dehydrogenation. The ketonic material obtained as described in the previous paragraph (5 c.c.) was heated with selenium (10 g.) at 280—310° for 24 hours. The product was extracted with ether and distilled at 10—11 mm. from a bath slowly heated from 155° to 190°, the final fractions being taken off at 0·1 mm. The violet distillate, which was partly crystalline, was treated with hexane and gave crystals of 4 : 7-dimethyl-2-*iso*propyl-5-indanol (IX) (0·75 g.). The violet hexane liquors were diluted with hexane, and the solution passed through a column of alumina. The violet zone was separated and eluted with alcohol, the solvent mostly evaporated, and the concentrated solution treated with *s*-trinitrobenzene (100 mg.). The crystalline product, recrystallised from alcohol, formed reddish-brown needles, m. p. 150—151·5°. This was the complex of vetivazulene (VIII), for which St. Pfau and Plattner (*Helv. Chim. Acta*, 1936, **19**, 871; 1939, **22**, 207) give m. p. 151·5° (Found: C, 61·5; H, 5·3; N, 10·3. Calc. for $C_{15}H_{18},C_6H_3O_6N_3$: C, 61·3; H, 5·15; N, 10·2%).

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