Studies in the Vitamin D Field. Part II. The Condensation of Acetylmethyl*cyclo*hexenes with* cyclo*Hexanone.*

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The condensation of 1-acetyl-2-methyl*cyclo*hexene (Ib) with *cyclo*hexanone, previously studied by Huber and by Turner and Voitle, has been re-investigated and found to give bicyclic as well as tricyclic products. Reduction of the bicyclic product (VI*b*) with lithium aluminium hydride yields the diethylenic alcohol (VII*b*). The monoallylic rather than diallylic structure of the latter is indicated by the relatively slow rate of its acid-catalysed anionotropic rearrangement which is accompanied by dehydration to diconjugated trienes and cyclisation. This approach does not, therefore, provide a useful route to the desired triconjugated trienes.

2-Acetyl-3-methyl*cyclo*hexene (I*c*) has been synthesised by an unambiguous method and has been found to undergo analogous reactions.

In Part I *, a new route to tachysterol analogues has been outlined. A possible alternative method of obtaining the diene alcohols required as intermediates consists of the selective reduction of the corresponding diene ketones. One such ketone (IV*b*) is theoretically accessible by the condensation of 1-acetyl-2-methyl*cyclo*hexene (I*b*) with *cyclo*hexanone. This reaction was first investigated by Huber (*Ber.*, 1938, **71**, 725) who, using potassium *iso*propoxide as catalyst, obtained as the sole product a tricyclic ketone regarded as (III*b*) and presumably formed *via* (II*b*) by successive Michael addition and internal condensation, as observed with 1-acetyl*cyclo*hexene (I*a*) (Rapson and Robinson, *J.*, 1935, 1285). More recently, the condensation of 1-acetyl-2-methyl*cyclo*hexene with *cyclo*hexanone under slightly different conditions (potassium *tert.*-butoxide) was re-investigated by Turner and Voitle (*J. Amer. Chem. Soc.*, 1950, **72**, 4166) who reported that the reaction did not furnish the tricyclic ketone, but gave a mixture of diethylenic ketones whose skeletal structure was proved to correspond to (IV*b*), though the position of the double bonds was not conclusively established.

In our hands, the condensation of 1-acetyl-2-methyl*cyclo*hexene, under Turner and Voitle's conditions, gave a mixture of bicyclic as well as tricyclic ketones. The tricyclic products are much higher-boiling than the bicyclic, and this may be the reason why Turner and Voitle failed to isolate them. The tricyclic nature of the high-boiling products followed from the fact that they contain only *one* ethylenic bond (microhydrogenation), but we have not investigated them fully since our interest was only in the bicyclic ketones. It may be noted, however, that Huber's evidence excludes neither prototropic nor skeletal isomers of (III*b*) and, indeed, the light-absorption properties and the difficulty of obtaining solid derivatives (see Experimental section) suggests that more than one tricyclic product is present.

The properties of the lower-boiling products agreed closely with those recorded by Turner and Voitle. The ultra-violet and infra-red light-absorption properties ($\lambda_{\text{max.}}$ 2470 Å, ε 5500; $\nu_{\text{max.}}$ 1680 cm.$^{-1}$) indicate a predominance of the monoconjugated ketone (VI*b*), the low intensity of the ultra-violet band being ascribed to steric hindrance to uniplanarity of the enone system, as in 1-acetyl-2-methyl*cyclo*hexene (I*b*) ($\lambda_{\text{max.}}$ 2450, ε 6500; $\nu_{\text{max.}}$ 1686 cm.$^{-1}$; Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890; Henbest and Woods, *J.*, 1952, 1150). The maximum of the diconjugated ketone (IV*b*) should be located near 2550 Å (cf. phorone, $\lambda_{\text{max.}}$ 2580 Å, ε 20,000 in EtOH), and although some (IV*b*) was probably present its proportion was evidently so low as to cause only band-broadening on the long-wave-length side.

Reduction of the ketone (VI*b*) with lithium aluminium hydride furnished the diethylenic

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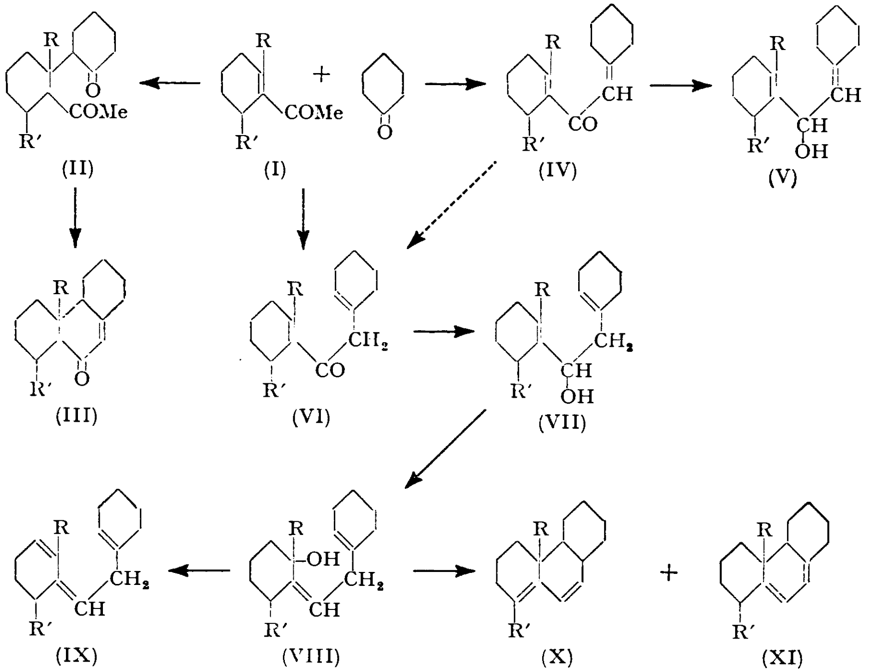
* Part I, preceding paper.

alcohol (VII*b*) which is transparent in the near-ultra-violet and undergoes no significant change in the presence of 0·001M-hydrogen chloride in aqueous dioxan at room temperature. This confirms that no appreciable amount of the diallylic alcohol (V*b*) which undergoes rapid anionotropic rearrangement under such conditions (Part I; cf. Braude, *Quart. Reviews*, 1950, **4**, 404) was present. As expected for a monoallylic alcohol, (VII*b*) was isomerised only under much more strongly acid conditions (0·1N-hydrogen chloride). Rearrangement to (VIII*b*) was accompanied by extensive dehydration and by the appearance of two absorption bands near 2400 and 2800 Å, the relative intensities of which were very dependent on the acid catalyst employed (see Experimental section). The two bands could be due, respectively, to the diconjugated * triene (IX*b*) and the corresponding triconjugated triene, the isolated double bond having been moved into the conjugated position under the influence of the acid catalyst. Microhydrogenation, however, showed the presence of only *two* double bonds indicating that acid-catalysed cyclisation had taken place and that the 2400-Å maximum belongs to a tricyclic diene (*e.g.*, X*b*) and the 2800-Å band to an isomeric tricyclic diene (XI*b*) containing the ergosterol type of chromophoric system. The formulations (X*b*) and (XI*b*) are supported both by the low intensities of the bands, and by the formation, presumably from (XI*b*), of a maleic anhydride adduct, isolated as the crystalline *N*-phenylimide.



(*a*, R = H, R′ = H; *b*, R = Me, R′ = H; *c*, R = H, R′ = Me.)

Since 1-acetyl-2-methyl*cyclo*hexene is known to undergo quite rapid prototropic isomerisation under the influence of metal alkoxides (cf. Braude *et al.*, *loc. cit.*, 1949), the corresponding sequence of reactions was, for comparison, carried through with 2-acetyl-3-methyl*cyclo*hexene (I*c*). This compound was obtained by Dimroth and Lüderitz (*Chem. Ber.*, 1947, **81**, 242), together with 1-acetyl-2-methyl*cyclo*hexene, by the treatment of 1-ethynyl-2-methyl*cyclo*hexanol with formic acid. The separation of the two products was, however, incomplete, and the assigned constitution was based solely on spectroscopic evidence. 2-Acetyl-3-methyl*cyclo*hexene has now been prepared by an unambiguous route, starting

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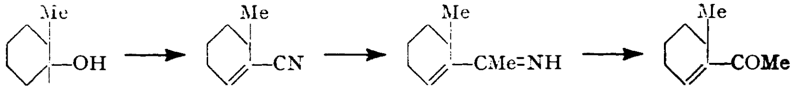
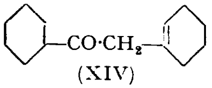
* Diconjugated and triconjugated refer to the structures having two and three double bonds in conjugation.

with the cyanohydrin of 2-methyl*cyclo*hexanone which was dehydrated by phosphorus oxychloride in pyridine to 2-cyano-3-methyl*cyclo*hexene (XII). The constitution of the latter was established by hydrolysis to 6-methyl*cyclo*hex-1-ene-1-carboxylic acid (Rapson and Shuttleworth, *J.*, 1940, 636) and by its ultra-violet light absorption ($\lambda_{max.}$ 2100, ε 9500), typical of the C:C·C:N system (cf. 1-cyano*cyclo*hexene, $\lambda_{max.}$ 2110 Å, ε 11,000; Part I, *loc. cit.*). Reaction of the cyanide with methylmagnesium iodide in benzene at 80°, followed by hydrolysis with dilute hydrochloric acid, gave the ketimine (XIII) characterised by a picrate. The ketimine shows a resistance to hydrolysis similar to that of aromatic ketimines (cf. Pickard *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 42; 1952, **74**, 4607; 1953, **75**, 5899; Culbertson, *ibid.*, 1951, **73**, 4818), but it is converted by hot hydrochloric or sulphuric acids into the ketone (I*c*) which was characterised by a semicarbazone. In contrast to 1-acetyl-3-methyl*cyclo*hexene, 2-acetyl-3-methyl*cyclo*hexene, and its derivatives exhibit almost normal spectroscopic properties, as would be expected since even in 2-acetyl-3 : 3-dimethyl*cyclo*hexene steric hindrance to the planarity of the conjugated enone system is only slight (Braude *et al.*, *loc. cit.*, 1949).


(XII) (XIII) (I*c*)

Condensation of 2-acetyl-3-methyl*cyclo*hexene with *cyclo*hexanone under the same conditions as those used for 1-acetyl-2-methyl*cyclo*hexene again gave two products differing widely in boiling point and shown by microhydrogenation to be diethylenic and monoethylenic, respectively. The higher-boiling monoethylenic, tricyclic ketone (III*c*) was not further investigated. Reduction of the lower-boiling, diethylenic, bicyclic ketone (VI*c*) gave the alcohol (VII*c*) which like the isomer (VII*b*) underwent rearrangement and dehydration on acid treatment to a mixture of readily oxidised hydrocarbons, probably mainly (X*c*) and (XI*c*).

For further comparison, the condensation of certain related ketones with *cyclo*hexanone under similar conditions has also been studied. Acetyl*cyclo*hexane gave the unconjugated *cyclo*hexenylacetyl*cyclo*hexane (XIV), characterised as the semicarbazone and 2 : 4-dinitrophenylhydrazone, together with a solid product, probably (XV) derived from 1 mol. of acetyl*cyclo*hexane and 2 mols. of *cyclo*hexanone. On the other hand, mesityl oxide which represents an acyclic analogue of acetylmethyl*cyclo*hexene, gives a diene ketone the spectral properties of which ($\lambda_{max.}$ 2950 Å, ε 14,500) show that it is not the cross-conjugated analogue (XVI), but must have either the structure (XVII) or (XVIII). The ultra-violet absorption makes (XVIII), which contains a *cisoid* enone grouping, more probable and it appears that the keto-group of mesityl oxide is relatively more reactive in this type of condensation than that of the acetyl*cyclo*hexenes.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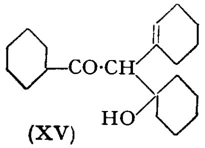
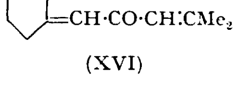
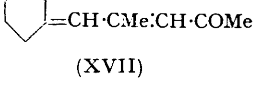
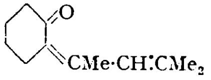

(XV)


(XVI)


(XVII)


(XVIII)

EXPERIMENTAL

For general methods, see Part I, *loc. cit.* Light-absorption data refer to ethanol solutions unless otherwise stated. Microhydrogenations were done in acetic acid, with platinic oxide as a catalyst.

Condensation of 1-*Acetyl*-2-*methyl*cyclo*hexene with* cyclo*Hexanone.*—1-Acetyl-2-methyl*cyclo*-

hexene (10 g.; n_{D}^{22} 1·869; $\lambda_{\max.}$ 2420 Å, ε 5500; prepared from either 1-methyl*cyclo*hexene or 1-ethynyl*cyclo*hexanol and purified by way of the semicarbazone as described by Braude *et al.*, *J.*, 1949, 1890), *cyclo*hexanone (7 g.), and dry pyridine (25 ml.) was added slowly to a solution prepared from potassium (3·5 g.), dry *tert.*-butanol (30 ml.), and ether (50 ml.). The mixture rapidly became homogeneous and assumed an orange colour, and a precipitate was slowly deposited. After 3 days at room temperature, water was added, the two layers were separated, the aqueous layer was acidified at 0° with hydrochloric acid and extracted with ether, and the combined ethereal solutions were washed with 2N-hydrochloric acid, 2N-sodium hydroxide, and water, and dried (Na_2SO_4). Distillation afforded two main fractions: (i) 1-cyclo*hex-1′-enylacetyl-2-methyl*cyclo*hexene* (8·0 g., 50%), b. p. 105—106°/0·005 mm., n_{D}^{20} 1·5164, $\lambda_{\max.}$ 2470 Å, ε 5500 (Found: C, 81·8; H, 10·2. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%. Microhydrogenation no. 94. Calc. for 2 double bonds, 109); (ii) a mixture of decahydromethyloxophenanthrenes (?) (3·5 g., 22%) which distilled as a very viscous oil, b. p. 90° (bath-temp.)/10^{-4} mm., n_{D}^{20} 1·5310, $\lambda_{\max.}$ 2360 ε 3400 (Found: C, 81·9; H, 10·3. Microhydrogenation no., 200. Calc. for one double bond, 218). The 2 : 4-dinitrophenylhydrazones prepared from both fractions were oils (cf. Huber, *Ber.*, 1938, **71**, 725; Turner and Voitle, *J. Amer. Chem. Soc.*, 1950, **72**, 4166).

Fraction (ii) was reduced with lithium aluminium hydride (0·75 g.) in ether at room temperature to give an *alcohol* (2·9 g., 80%) which distilled as an extremely viscous glass, b. p. 100° (bath-temp.)/10^{-4} mm. (Found: C, 81·5; H, 11·3. $C_{15}H_{24}O$ requires C, 81·8; H, 11·0%), and gave an oily 3 : 5-dinitrobenzoate (cf. Huber, *loc. cit.*).

2-cyclo*Hex-1′-enyl-1-(2-methyl*cyclo*hex-1-enyl)ethanol* (VII*b*).—1-*cyclo*Hex-1′-enylacetyl-2-methyl*cyclo*hexene (8·0 g.) in ether (100 ml.) was reduced with lithium aluminium hydride (1·6 g.) in ether (100 ml.) at −25°. After hydrolysis with aqueous ammonium chloride, the ether layer was separated, dried (Na_2SO_4–K_2CO_3), and distilled, giving the *alcohol* as a colourless, very viscous oil (7·3 g., 90%), b. p. 105—107°/10^{-3} mm., n_{D}^{25} 1·5170, ε < 1000 at 2470 Å (Found: C, 81·5; H, 11·2%).

Acid Treatment of the Alcohol (VII*b*).—(i) Preliminary experiments were carried out by adding 0·1 ml. of a stock solution of the foregoing alcohol (1·85 mg.) in purified dioxan (10 ml.) to solutions of hydrogen chloride in 60% aqueous dioxan (2·5 ml.) contained in the 1-cm. cell of a Unicam S.P.500 spectrophotometer and observing the change in ultra-violet light absorption (cf. Barany, Braude, and Coles, *J.*, 1951, 2093). No significant change was observed with 0·001M-hydrochloric acid during 24 hr. at 25°, and only very slow change with 0·01M-acid. With 0·1M-acid, the following results, typical of several runs, were obtained:

Time (min.)	0	25	50	75	90	120	235
ε_{2400} (Å)	120	1600	3000	4300	5100	6300	9500
ε_{2800} (Å)	50	1200	1400	1700	1800	2000	2500

(ii) The alcohol (6 g.) was dissolved in a 0·1M-solution of hydrogen chloride in 80% aqueous acetone. An oil separated slowly from the initially homogeneous mixture. After 12 hr. at room temperature, the acid was neutralised with potassium carbonate and most of the acetone removed under reduced pressure. Extraction of the residue with ether and distillation gave a *diene* (5·2 g.), b. p. 92—94°/10^{-2} mm., n_{D}^{23} 1·5380, $\lambda_{\max.}$ 2400 Å (ε 13,000) and 2780 Å (ε 5000) which avidly absorbed oxygen (Found: C, 86·7; H, 11·0. $C_{15}H_{22}$ requires C, 89·0; H, 11·0. Microhydrogenation number, 113. Calc. for two double bonds, 101). The physical properties and composition underwent little change on redistillation from powdered potassium hydrogen sulphate or in the presence of iodine.

(iii) The alcohol (1·2 g.), naphthalene-β-sulphonic acid (0·1 g.), and dry benzene (15 ml.) were refluxed for 30 min. under nitrogen. After cooling, the solution was washed with water, dried (Na_2SO_4), and distilled, giving a *diene* (0·8 g.), b. p. 100°/10^{-2} mm., n_{D}^{26} 1·5480, $\lambda_{\max.}$ 2400 Å, (ε 4000) and 2800 (ε 9000) (Found: C, 87·0; H, 10·8. $C_{15}H_{22}$ requires C, 89·0; H, 11·0%). No formaldehyde could be detected on ozonisation in acetic acid. Heating the diene (1·0 g.) with maleic anhydride (0·4 g.) in xylene (2 ml.) for 2 hr. under reflux gave an oil converted by aniline at 90° in 1 hr. (cf. Conroy, *J. Amer. Chem. Soc.*, 1952, **74**, 3046) into the N-*phenylmaleimide* adduct (70 mg.) which crystallised from aqueous methanol in plates, m. p. 194° (Found: C, 78·9; H, 7·6; N, 4·3; O, 9·55. $C_{25}H_{29}NO_2,\frac{1}{3}H_2O$ requires C, 78·9; H, 7·8; N, 3·7; O, 9·8%).

2-*Acetyl-3-methyl*cyclo*hexene* (I*c*).—Liquid hydrogen cyanide (100 ml.) and a few crystals of potassium cyanide were added to 2-methyl*cyclo*hexanone (135 g.), and the mixture kept in a stoppered flask for 2 days at room temperature. Syrupy phosphoric acid (2 ml.) was then added until the mixture was acid to methyl-orange. The excess of hydrogen cyanide was removed under reduced pressure, and the residue distilled, giving unchanged ketone (20 g.), b. p. 55—

58°/0·2 mm., and the cyanohydrin (128 g.), b. p. 70—72°/0·5 mm., n_D^{21} 1·4640 (Linstead and Millidge, *J.*, 1936, 482, give b. p. 122°/10 mm.). The cyanohydrin was also prepared, in similar yield, by adding concentrated hydrochloric acid to a mixture of ketone and potassium cyanide below 0° (cf. Billimoria and Maclagan, *J.*, 1951, 3069).

The cyanohydrin (25 g.) was dehydrated by treatment with phosphorus oxychloride (30 ml.) and dry pyridine (30 ml.), the reactants being mixed at 0° and then kept at 20° for 20 min. and finally at 90° for 30 min. After cooling, ice was added and the ethereal layer was separated, washed with hydrochloric acid, dried, and distilled, giving 2-cyano-3-methyl*cyclo*hexene (17 g., 77%), b. p. 78°/10 mm., n_D^{21} 1·4782, $\lambda_{max.}$ 2100 Å, ε 9500 (Linstead and Millidge, *loc. cit.*, give b. p. 86°/10 mm.). A small portion was hydrolysed by heating with phosphoric acid (90%) at 130—140° for 5 hr. to 6-methyl*cyclo*hex-1-ene-1-carboxylic acid, m. p. 104°, $\lambda_{max.}$ 2160 Å, ε 10,500 (Rapson and Shuttleworth, *J.*, 1940, 636, give m. p. 105°).

Methylmagnesium iodide (from Mg, 3 g., and MeI, 20 g.) was prepared in ether (50 ml.), benzene (50 ml.) was added, and the ether distilled off by heating until the vapour temperature reached 70°. 2-Cyano-3-methyl*cyclo*hexene (10 g.) was then added at 20° and the mixture refluxed for 6 hr. (cf. Haworth and Mavin, *J.*, 1932, 2720; Fieser and Seligman, *J. Amer. Chem. Soc.*, 1936, **58**, 2482). After cooling, excess of aqueous ammonium chloride was added and the ether layer was separated and extracted with 5% aqueous sulphuric acid at 0°. The acidic extract was immediately poured into excess of aqueous ammonia and the oil which separated was taken up in ether and dried (Na_2SO_4). Distillation gave the unstable 2-*acetyl*-3-*methyl*cyclo*hexene ketimine* (5·9 g., 58%), b. p. 38°/0·2 mm., n_D^{24} 1·4975, $\lambda_{max.}$ 2270 Å, ε 5500 (Found: C, 78·5; H, 11·2; N, 9·8. $C_9H_{15}N$ requires C, 78·8; H, 11·0; N, 10·2%). The *picrate* crystallised from benzene in plates which had a double m. p. 112° and 122° (Found: C, 48·5; H, 5·3; N, 15·9. $C_{15}H_{18}O_7N_4$ requires C, 49·2; H, 5·0; N, 15·3%).

Hydrolysis of the ketimine (4·0 g.) was effected by heating with N-sulphuric acid (100 ml.) and benzene (20 ml.) under reflux for 15 min. Distillation of the benzene layer gave 2-*acetyl*-3-*methyl*cyclo*hexene* (3·1 g.), b. p. 90°/15 mm., n_D^{20} 1·4875, $\lambda_{max.}$ 2340 Å, ε 11,000 (Found: C, 77·5; H, 10·2. $C_9H_{14}O$ requires C, 78·2; H, 10·2%) (Dimroth and Lüderitz, *loc. cit.*, give $\lambda_{max.}$ 2380 Å, ε 8300, but no analytical data). The *semicarbazone* was crystallised from ethanol and had m. p. 204°, $\lambda_{max.}$ 2580 Å, ε 22,000 (Found: C, 61·7; H, 8·6; N, 21·1. $C_{10}H_{17}ON_3$ requires C, 61·5; H, 8·8; N, 21·5%) (Dimroth and Lüderitz, *loc. cit.*, give m. p. 208° for a derivative which was formulated as a pyrazoline but was almost certainly the semicarbazone; cf. Braude *et al.*, *J.*, 1949, 1890). The 2 : 4-*dinitrophenylhydrazone* was chromatographed on alumina in benzene and crystallised from methanol in plates, m. p. 132°, $\lambda_{max.}$ 3860 Å, ε 23,000 in $CHCl_3$ (Found: C, 56·7; H, 5·9; N, 17·8. $C_{15}H_{18}O_4N_4$ requires C, 56·6; H, 5·7; N, 17·6%).

In subsequent experiments, the ketone was obtained directly from the Grignard reaction mixture by hydrolysis with concentrated hydrochloric acid (5 ml.) at 80° for 20 min. The yield was 6·8 g. (63%). When the time of reflux with methylmagnesium iodide was reduced to 1 hr., the yield dropped to 38%. Mainly unchanged nitrile and a very low yield of ketone (5%, isolated as the semicarbazone) were obtained from a Grignard reaction in refluxing ether. No appreciable reaction took place in ether at room temperature.

Condensation of 2-*Acetyl*-3-*methyl*cyclo*hexene with* cyclo*Hexanone*.—2-Acetyl-3-methyl*cyclo*hexene (8·1 g.) was condensed with *cyclo*hexanone (6·4 g.) under the same conditions as described above for 1-acetyl-2-methyl*cyclo*hexene. Two main products were obtained: (i) 2-cyclo*hex*-1′-*enylacetyl*-3-*methyl*cyclo*hexene* (6 g., 46%), b. p. 97°/10⁻³ mm., n_D^{18} 1·5240, $\lambda_{max.}$ 2430 Å, ε 5700 (Found: C, 82·4; H, 10·2. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%); and (ii) a mixture of decahydromethyloxophenanthrenes (?) (2·5 g., 19%), which distilled as a very viscous glass, b. p. 100° (bath-temp.)/5 × 10⁻⁴ mm., showing diffuse absorption through the 2300—2600-Å region (ε 2000—3000) (Found: C, 80·5; H, 10·2%).

2-cyclo*Hex*-1′-*enyl*-1-(6-*methyl*cyclo*hex*-1-*enyl*)*ethanol* (VII*c*).—2-*cyclo*Hex-1′-enylacetyl-3-methyl*cyclo*hexene (4·4 g.) was reduced with lithium aluminium hydride (0·9 g.) in ether (60 ml.) at −20°. Working up as above gave the *alcohol* as viscous oil (4·0 g.), b. p. 98°/10⁻³ mm., n_D^{22} 1·5230, ε <1000 at 2400 Å (Found: C, 81·4; H, 11·1. $C_{15}H_{24}O$ requires C, 81·8; H, 11·0%).

Acid Treatment of the Alcohol (VII*c*).—(i) Preliminary spectrometric experiments were carried out as described above for (VII*b*). A typical run in 0·1M-hydrogen chloride in 60% aqueous dioxan at 20° was as follows:

Time (min.)	25	50	90	135	240
ε_{2380} (Å)	2700	3500	4500	5400	6800
ε_{2800} (Å)	1300	1600	1800	2000	2300

(ii) The alcohol (3·5 g.) was dissolved in 0·1M-hydrogen chloride in 80% aqueous acetone (200 ml.), and the mixture kept at room temperature for 18 hr. Isolation of the product as previously gave a viscous oil (2·9 g.), b. p. 88°/10^{-3} mm., n_D^{20} 1·5338, $\lambda_{max.}$ 2380 (ε 9000) and 2800 Å (ε 3000) (Found : C, 85·5; H, 11·0. $C_{15}H_{22}$ requires C, 89·0; H, 11·0%). Redistillation from potassium hydrogen sulphate gave a *diene* (1·7 g.), b. p. 88°/10^{-3} mm., n_D^{22} 1·5335 (Found : C, 86·3; H, 11·0. Microhydrogenation no. 98. Calc. for 2 double bonds, 101), which rapidly absorbed oxygen (Found : O, 6·2% after 4 hr.; 7·6% after 20 hr.). The oxygen was only partly removed by distillation from zinc dust (Found : C, 85·5; H, 11·0; O, 3·5%).

*Condensation of Acetyl*cyclo*hexane with* cyclo*Hexanone.*—Acetyl*cyclo*hexene (prepared by the method of Deno and Chafetz, *J. Amer. Chem. Soc.*, 1952, **74**, 3940) was hydrogenated in ethyl acetate in the presence of platinic oxide. Distillation gave acetyl*cyclo*hexane, b. p. 70°/12 mm., n_D^{19} 1·4525 (Wieland and Bettag, *Ber.*, 1922, **55**, 2246, give b. p. 74—77°/10 mm.). The 2 : 4-dinitrophenylhydrazone was chromatographed on alumina in benzene and crystallised from ethyl acetate in orange prisms, m. p. 140°, $\lambda_{max.}$ 3680 Å, ε 22,000 in $CHCl_3$ (Found : C, 55·0; H, 6·1; N, 18·1. Calc. for $C_{14}H_{18}O_4N_4$: C, 54·9; H, 5·9; N, 18·3%) (Hughes and Lions, *Proc. Roy. Soc. New South Wales*, 1938, **41**, 494, give m. p. 128°).

Acetyl*cyclo*hexane (6 g.) and *cyclo*hexanone (5 g.) in pyridine (20 ml.) were added to a solution of potassium *tert.*-butoxide (from K, 2·2 g.) in dry *tert.*-butanol (20 ml.) and ether (50 ml.). After 6 days at room temperature, the mixture was worked up in the usual manner and yielded a solid product (4·6 g.) and an oil (2·8 g.). The oil was distilled, giving cyclo*hex*-1′-*enylacetyl*cyclo*hexane*, b. p. 76°/10^{-3} mm., n_D^{20} 1·5002 (Found : C, 81·0; H, 10·6. $C_{14}H_{22}O$ requires C, 81·5; H, 10·75%). The *semicarbazone* crystallised from aqueous ethanol as needles, m. p. 174°, $\lambda_{max.}$ 2280 Å, ε 13,000 (Found : C, 68·4; H, 9·8; N, 16·1. $C_{15}H_{25}ON_3$ requires C, 68·4; H, 9·6; N, 16·0%). The 2 : 4-*dinitrophenylhydrazone* was chromatographed on alumina in benzene and crystallised from ethyl acetate as yellow prisms, m. p. 102°, $\lambda_{max.}$ 3710 Å, ε 22,000 in $CHCl_3$ (Found : C, 61·8; H, 6·8; N, 14·4. $C_{20}H_{26}O_4N_4$ requires C, 62·1; H, 6·8; N, 14·5%). The solid, formulated as α-cyclo*hex*-1-*enyl*-α-(1-*hydroxy*cyclo*hexyl*)*acetyl*cyclo*hexane* (XV) crystallised from ethyl acetate as needles, m. p. 192°, unchanged after sublimation at 160—180°/0·5 mm. (Found : C, 78·9, 79·1; H, 10·7, 10·7. $C_{20}H_{32}O_2$ requires C, 78·9; H, 10·6%). Ultra-violet light absorption : ε <500 between 2200 and 4000 Å. Infra-red light absorption : $\nu_{max.}$ 1695 cm.$^{-1}$ (ε *ca.* 300, CO stretching) in $CHCl_3$ (10%; NaCl prism) and 3597 cm.$^{-1}$ (ε *ca.* 40, O–H stretching) in CCl_4 (2·5%; LiF prism).

Condensation of Mesityl Oxide with cyclo*Hexanone.*—Mesityl oxide (9·8 g.) was condensed with *cyclo*hexanone (9·8 g.) under the conditions described above for acetylmethyl*cyclo*hexene. Distillation of the products afforded unchanged *cyclo*hexanone (1·5 g.) and 2-(1 : 3-*dimethylbut*-2-*enylidene*)cyclo*hexanone* (?) (6·0 g., 32%), b. p. 75°/0·1 mm., n_D^{19} 1·5220, $\lambda_{max.}$ 2950 Å, ε 14,500, $\lambda_{infl.}$ 3040 Å, ε 13,500 (Found : C, 80·5; H, 10·2. $C_{12}H_{18}O$ requires C, 80·9; H, 10·2%). The 2 : 4-*dinitrophenylhydrazone* was chromatographed on alumina in benzene and crystallised from ethyl acetate as purple needles, m. p. 168° $\lambda_{max.}$ 3070 (ε 16,500) and 4150 Å (ε 27,000), $\lambda_{infl.}$ 4500 Å (ε 20,000) in $CHCl_3$ (Found : C, 60·8; H, 6·6; N, 15·4. $C_{18}H_{22}O_4N_4$ requires C, 60·3; H, 6·2; N, 15·6%).

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