157. *Studies in the Polyene Series. Part XXVI. The Synthesis of Analogues of β-Ionone.*

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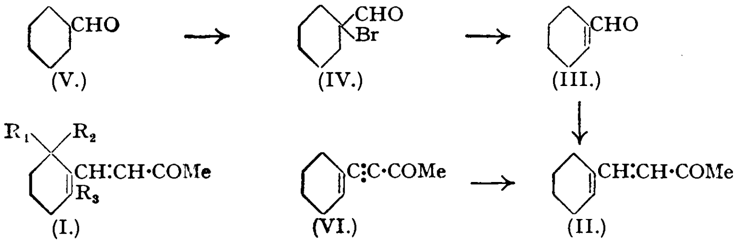
New methods have been devised for the preparation of *cyclo*hexenealdehyde (III) and 2-methyl*cyclo*hex-1-enealdehyde (X). Condensation of these aldehydes with acetone gave simple analogues of *β*-ionone (I; $R_1 = R_2 = R_3 =$ Me) which are now readily available. These ketones are required for synthetic studies in the vitamin-A series and also for the elucidation of certain anomalies in the light-absorption properties of *β*-ionone.

THE importance of β-ionone (I; $R_1 = R_2 = R_3 = $ Me) as a starting material for the synthesis of polyenes of the vitamin-A and carotenoid types has long been recognised, and its usefulness for this purpose has been demonstrated in recent successful syntheses (*inter al.*, Isler, Huber, Ronco, and Kofler, *Helv. Chim. Acta*, 1947, **30**, 1911; Arens and van Dorp, *Rec. Trav. chim.*, 1946, **65**, 338; *Nature*, 1947, **160**, 189; Heilbron, Jones, and O'Sullivan, *J.*, 1946, 866). As has already been indicated (Heilbron, *J.*, 1948, 386; Heilbron, Jones, and Richardson, this vol., p. 287) work is in progress in these laboratories with the object of producing compounds with modified vitamin-A structures, with a view to elucidating the relationship between structure and physiological activity.

The scheme, which is being followed, consists in the progressive introduction of methyl groups into a basic vitamin-A structure entirely devoid of such groups. For this purpose it was necessary to devise convenient methods for the synthesis of analogues of β-ionone of the type (I; $R_1, R_2, R_3 = $ H or Me), and this paper describes the synthesis of two such analogues (II) and (VII). Such compounds are also of interest in other connexions. Thus it has been found by various workers (cf. Jones, *Ann. Reports*, 1941, **38**, 180) that β-ionone behaves anomalously in Grignard type reactions, and the behaviour of these simple analogues in reactions of this type will be studied. Furthermore we have been interested for a long time in the elucidation of the reasons for certain anomalies in the light-absorption properties of β-ionone and related substances: the data obtained from measurements with these simplified compounds have made possible the solution of this problem (forthcoming publication).

Two different methods for the preparation of these unsaturated ketones have been developed:

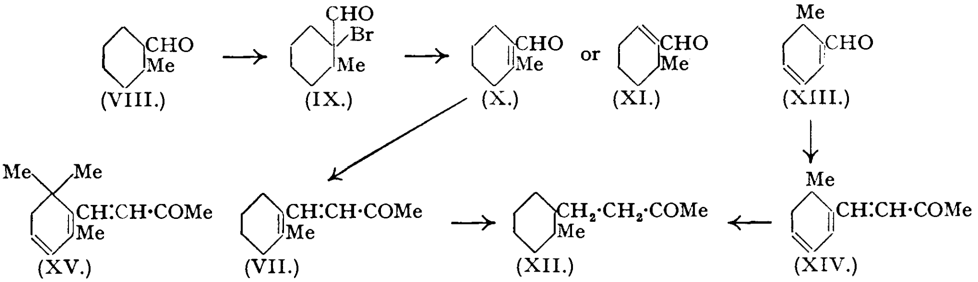


*cyclo*Hexenealdehyde (III), the obvious precursor of (II), has been obtained previously only in small quantities in poor yields (Wallach and Isaac, *Annalen*, 1906, **347**, 328; Borsche and Schmidt, *Ber.*, 1910, **43**, 3400; Plattner and Jampolsky, *Helv. Chim. Acta*, 1943, **26**, 687; Venus-Danilova, *J. Gen. Chem. Russia*, 1936, **6**, 1863). It has now been prepared in reasonable yield from *cyclo*hexanealdehyde (V), which was made most conveniently by the hydrogenation of *cyclo*hex-3-enealdehyde (from butadiene and acraldehyde) (cf. Diels and Alder, *Annalen*, 1928, **460**, 98, who hydrogenated the semicarbazone). *cyclo*Hexanealdehyde (V) was brominated with bromine in chloroform by the method of Barbier (*Helv. Chim. Acta*, 1940, **23**, 793; cf. Venus-Danilova, *loc. cit.*) to give an 80% yield of the bromo-aldehyde (IV). This was conveniently dehydrobrominated by heating with an excess of diethylaniline at 100° for 14—54 hours (depending on the scale of the experiment), to give (III) in 75% yield. Alternatively the bromo-aldehyde was converted into the semicarbazone of (III) by the method of Barbier (*loc. cit.*), *i.e.* heating with excess of semicarbazide acetate. In the latter case the overall yield of (III) from (V) was, however, only *ca.* 35%. When (III) was condensed with acetone in the presence of sodium hydroxide, the required 4-*cyclohex-1'-enylbut-3-en-2-one* (II) was obtained together with unchanged aldehyde. The latter was again condensed with acetone to give a total yield of 60% of the analogue (II), which is now obtainable in large quantities in an overall yield of *ca.* 30% based on acraldehyde. The structure of the ketone was confirmed by hydrogenation and by ozonolysis, whereby a 55% yield of adipic acid was obtained. For spectrographic purposes, the ketone was characterised by a number of derivatives, the *semicarbazone*, *phenylsemicarbazone*, *thiosemicarbazone*, and 2 : 4-*dinitrophenylhydrazone* being prepared.

The analogue (II) was also made by the partial hydrogenation of the acetylenic ketone (VI), the preparation of which has already been described (Heilbron, Jones, and Richardson, *loc. cit.*). When this was hydrogenated in the presence of a quinoline-poisoned palladium–charcoal catalyst (cf. Isler, Huber, Ronco, and Kofler, *Experientia*, 1946, **2**, 31; *Helv. Chim. Acta*, *loc. cit.*), and the hydrogenation interrupted at the appropriate stage, the ketone (II) could be isolated as its semicarbazone in 20% yield.

The homologous ketone (VII) was also prepared by a similar method. 2-Methyl*cyclo*-

hexanealdehyde (VIII), prepared by hydrogenation of the Diels–Alder adduct of butadiene and crotonaldehyde (Diels and Alder, *Annalen*, 1929, **470**, 62), was brominated as before to give an 80% yield of the rather unstable *bromo-aldehyde* (IX). Little dehydrobromination occurred when this was heated with semicarbazide acetate solution or with diethylaniline at 100°. However when the bromo-aldehyde was heated to boiling with diethylaniline for 2 minutes, the crude product on treatment with semicarbazide acetate gave a 40% yield of 2-*methyl*cyclo*hex*-1-*enealdehyde semicarbazone*, which on steam distillation in the presence of oxalic acid yielded the *aldehyde* (X). That this compound had structure (X) and not (XI) was shown by the fact that the aldehyde, its semicarbazone, and its 2 : 4-dinitrophenylhydrazone were different from the previously-prepared isomer (XI) and its derivatives (Rapson and Shuttleworth, *J.*, 1940, 636). Further the melting point of the 2 : 4-dinitrophenylhydrazone was in agreement with that previously recorded (Howton, *J. Org. Chem.*, 1947, **12**, 379) for the derivative of an aldehyde believed to be (X). Final confirmation of the structure (X) was provided by oxidation of the aldehyde with silver oxide to 2-methyl*cyclo*hex-1-enecarboxylic acid. No rearrangement could have occurred during the oxidation, as Rapson and Shuttleworth (*loc. cit.*) obtained the isomeric 6-methyl*cyclo*hex-1-enecarboxylic acid by oxidation of the isomer (XI) under similar conditions.



When the aldehyde (X) was condensed with acetone in the presence of aqueous sodium hydroxide, the *ketone* (VII) was obtained in 63% yield; it was characterised by the formation of a *semicarbazone* and 2 : 4-*dinitrophenylhydrazone*. On hydrogenation it gave the saturated *ketone* (XII) (*semicarbazone* and 2 : 4-*dinitrophenylhydrazone*), which was obtained independently as described later.

When dihydro-*o*-tolualdehyde (XIII) (Bernhauer *et al.*, *Biochem. Z.*, 1932, **251**, 173; *Annalen*, 1936, **525**, 43) was condensed with acetone, the triply unsaturated *ketone* (XIV) (*semicarbazone* and 2 : 4-*dinitrophenylhydrazone*) was obtained in 50% yield. This is of interest because of its close relationship with dehydro-β-ionone (XV) recently prepared in these laboratories (Henbest, *Nature*, 1948, **161**, 481). On hydrogenation (XIV) gave the same saturated ketone (XII) as had been obtained above.

The light-absorption data of the compounds described in this paper are recorded in the Experimental section, and will be discussed, together with those of related compounds, in a forthcoming publication.

EXPERIMENTAL.

(All light-absorption data were determined in alcoholic solution unless stated otherwise.)

cyclo*Hexanealdehyde* (V).—*cyclo*Hex-3-enealdehyde (338 g.), prepared in 90% yield from acraldehyde and butadiene by the method of Diels and Alder (*Annalen*, 1928, **460**, 98; see also Chayanov, *J. Gen. Chem. Russia*, 1938, **8**, 460), was dissolved in methanol (650 c.c.), and the solution was shaken for some hours with Raney nickel. The filtered liquid and a pre-reduced palladium–calcium carbonate catalyst (20 g.; 10% $PdCl_2$) were shaken in hydrogen at atmospheric pressure until absorption was complete (73 l. of hydrogen absorbed, corresponding to 1·0 |=). The filtrate was evaporated, and distillation gave *cyclo*hexanealdehyde (296 g.; 86%), b. p. 61—63°/24 mm., $n_D^{18^\circ}$ 1·4503 (Wallach and Isaac, *loc. cit.*, give b. p. 161—163°, $n_D^{19^\circ}$ 1·4495). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in yellow plates, m. p. 172° (Found : N, 19·5. $C_{13}H_{16}O_4N_4$ requires N, 19·2%). The aldehyde has also been prepared from *cyclo*hexyl bromide by the method of Wood and Comley (*J. Soc. Chem. Ind.*, 1923, **42**, 429), but the procedure described above is much better.

cyclo*Hexenealdehyde* (III).—The saturated aldehyde (245 g.) in chloroform (800 c.c.), together with finely-powdered calcium carbonate (150 g.), was cooled to 0° and stirred while a solution of bromine (350 g.) in chloroform (300 c.c.) was added slowly. After being stirred overnight at room temperature the mixture was filtered, and the filtrate was washed with sodium hydrogen carbonate solution and sodium thiosulphate. The solvent was evaporated from the dried solution, and distillation gave 1-bromo*cyclo*hexanealdehyde (331 g.; 80%), b. p. 90—91°/20 mm., $n_D^{18^\circ}$ 1·500. The bromo-aldehyde (330 g.) and diethylaniline (600 g.) were heated on the steam-bath in nitrogen for 14 hours. Water and ether were added, and the excess of diethylaniline was removed by washing with dilute sulphuric acid. Removal of the solvent from the dried extract left a residue which still contained a considerable amount of bromo-aldehyde. It was therefore heated with more diethylaniline (600 g.) on the steam-bath for a further 40 hours. Isolation as before, followed by distillation, gave *cyclo*hexenealdehyde (146 g.; 77%), b. p. 70°/13 mm., $n_{\rm D}^{17^\circ}$ 1·4921 (Venus-Danilova, *loc. cit.*, gives b. p. 61—63°/10 mm.). Light absorption : Maximum, 2290 A.; ε = 12,100. In a small-scale experiment (11 g. of bromo-aldehyde and 20 g. of diethylaniline) dehydrobromination was complete after 14 hours. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in light red needles, m. p. 219—220° (Found : N, 19·5. $C_{13}H_{14}O_4N_4$ requires N, 19·3%). Light absorption (in chloroform) : Maximum, 3770 A.; ε = 27,800.

Alternatively the crude, undistilled bromo-aldehyde (from 12·5 g. of *cyclo*hexanealdehyde) was treated with a solution of semicarbazide acetate (from the hydrochloride, 20 g.) in alcohol (85 c.c.) and water (50 c.c.), kept at 20° for 15 hours and then heated under reflux for 1 hour. Dilution with water and cooling gave the semicarbazone of the unsaturated aldehyde (9·5 g.) in a fairly pure condition, m. p. 200—205°, raised to 213—214° by crystallisation from methanol (Plattner and Jampolsky, *loc. cit.*, give m. p. 213—216°). Light absorption : Maxima, 2600, 2650 A.; ε = 28,500 and 31,700 respectively. The aldehyde was regenerated by steam distillation of the crude semicarbazone with oxalic acid (15 g.) and isolated *via* ether. Removal of the ether through a column gave *cyclo*hexenealdehyde (4·3 g.), $n_{\rm D}^{22^\circ}$ 1·492.

4-cyclo*Hex*-1′-*enylbut*-3-*en*-2-*one* (II).—A solution of *cyclo*hexenealdehyde (130 g.) in acetone (250 c.c.) was added during 15 minutes to a well-stirred solution of sodium hydroxide (12·5 g.) in a mixture of acetone (1000 c.c.) and water (400 c.c.) at 0°. The mixture was allowed to warm to room temperature during 45 minutes, and was then stirred for a further hour. It was poured into water (3 l.) containing excess of sulphuric acid, and the product was isolated with ether. The ether extract was thoroughly washed with water, dried, and evaporated. Distillation of the residue gave 4-cyclo*hex*-1′-*enylbut*-3-*en*-2-*one* (80 g.) and unchanged aldehyde (55 g.); the latter was again condensed with acetone, and another 26 g. of ketone were obtained. The total yield of ketone was 60% (106 g.), b. p. 64°/0·1 mm., 131—132°/14 mm., $n_{\rm D}^{23^\circ}$ 1·5492 (Found : C, 79·65; H, 9·35. $C_{10}H_{14}O$ requires C, 79·95; H, 9·4%). Light absorption : Maximum, 2810 A.; ε = 20,800. The ketone had an odour resembling that of β-ionone. Another sample of the ketone, regenerated from the semicarbazone (see later) by heating under reflux with stirring for 1·5 hours with 2N-sulphuric acid and light petroleum (b. p. 80—100°), had b. p. 63°/0·2 mm., $n_{\rm D}^{22^\circ}$ 1·5490.

The *semicarbazone* crystallised from ethanol–ethyl acetate in long prismatic needles, m. p. 208—209° (Found : N, 20·05. $C_{11}H_{17}ON_3$ requires N, 20·3%). Light absorption : Maximum, 2900 A.; ε = 35,000. Inflexion, 3000 A.; ε = 32,000. The *phenylsemicarbazone* separated from ethyl acetate as colourless needles, m. p. 211° (decomp.), which became yellow on exposure to air and light (Found : N, 14·35. $C_{17}H_{21}ON_3$ requires N, 14·85%). Light absorption : Maximum, 3000 A.; ε = 41,000. Inflexion, 3070 A.; ε = 37,000. The *thiosemicarbazone* crystallised from aqueous methanol in pale yellow-brown leaflets, m. p. 174° (Found : N, 19·15. $C_{11}H_{17}SN_3$ requires N, 18·8%). Light absorption : Maximum, 3180 A.; ε = 39,000. Inflexion, 3290 A.; ε = 35,000. The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate as dark red, lustrous prisms, m. p. 196° (Found : C, 58·3; H, 5·6. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·5%). Light absorption (in chloroform) : Maximum, 3950 A.; ε = 32,000.

4-cyclo*Hexylbutan*-2-*one*.—A solution of the ketone (II) (0·25 g.) in methanol (10 c.c.) together with some platinic oxide catalyst was shaken with hydrogen until absorption was complete (hydrogen absorbed, 80 c.c. at 27°/753 mm., equivalent to 1·95 |=). The saturated ketone was converted into its semicarbazone (0·25 g.), which after crystallisation from aqueous methanol had m. p. 163°, undepressed on admixture with an authentic specimen (Heilbron, Jones, and Richardson, *loc. cit.*).

Ozonolysis of 4-cyclo*Hex*-1′-*enylbut*-3-*en*-2-*one*.—Ozonised oxygen was passed into a solution of the ketone (0·35 g.) in glacial acetic acid (10 c.c.) at 20° until a quantity approximately 50% in excess of that calculated had been absorbed. Hydrogen peroxide (20 c.c.; 50 vol.) was added, and after 24 hours the solution was boiled under reflux for 2 hours. Evaporation under reduced pressure gave a crude solid product (0·32 g.) which after crystallisation from 50% nitric acid gave adipic acid, m. p. 145—146°, undepressed on admixture with an authentic specimen.

Preparation of 4-cyclo*Hex*-1′-*enylbut*-3-*en*-2-*one* (II) *by Partial Hydrogenation of* 4-cyclo*Hex*-1′-*enylbut*-3-*yn*-2-*one* (VI).—The acetylenic ketone (10 g.; Heilbron, Jones, and Richardson, *loc. cit.*) was dissolved in pure methanol (75 c.c.) and, together with quinoline-poisoned palladium–charcoal (1 g.; prepared by the method of Isler, Huber, Ronco, and Kofler, *Experientia, loc. cit.*; *Helv. Chim. Acta, loc. cit.*) was shaken with hydrogen at 20°/761 mm. until the calculated quantity of hydrogen (1620 c.c.) had been absorbed. The catalyst was filtered off, the bulk of the methanol was removed through a column, and the residue, dissolved in ether, was shaken successively with N-sulphuric acid, sodium hydrogen carbonate solution, and water. After evaporation of the dried ethereal solution, the product was distilled, and the fraction (4·1 g.), with b. p. 60—65°/0·5 mm., $n_{\rm D}^{25^\circ}$ 1·535, was treated with semicarbazide acetate. The crude derivative (3·5 g.), m. p. 199—201°, was crystallised from alcohol–ethyl acetate to give 4-*cyclo*hex-1′-enylbut-3-en-2-one semicarbazone (2·5 g.), m. p. 205—207°, undepressed on admixture with a specimen prepared by the alternative route described above.

1-*Bromo*-2-*methyl*cyclo*hexanealdehyde* (IX).—2-Methyl*cyclo*hexanealdehyde (22 g.; Diels and Alder, *Annalen*, 1929, **470**, 62) in chloroform (70 c.c.), together with finely-powdered calcium carbonate (14 g.), was cooled to 10° and stirred while a solution of bromine (28 g.) in chloroform (25 c.c.) was added slowly. After being stirred for a further 3 hours at room temperature, the mixture was filtered, and the solvent was removed under reduced pressure. Distillation of the residue gave 1-*bromo*-2-*methyl*cyclo*hexanealdehyde* (28·7 g.; 80%) as a colourless unstable liquid, b. p. 74—78°/0·7 mm., $n_{\rm D}^{18^\circ}$ 1·498 (Found : C, 47·35; H, 6·65. $C_8H_{13}OBr$ requires C, 46·85; H, 6·4%).

2-*Methyl*cyclo*hex*-1-*enealdehyde* (X).—The bromo-aldehyde (28·5 g.) and diethylaniline (60 g.) were heated to boiling in nitrogen. The solution was heated under reflux for 2 minutes, and was then rapidly cooled (if heating is prolonged much self-condensation of the aldehyde occurs). Working up as before gave a liquid (13·3 g.) which could not be obtained pure by distillation. A solution of semicarbazide acetate was added, and the solid which separated was crystallised from methoxyethanol. This gave the *semicarbazone* of (X) (9·9 g.; 40% based on the bromo-aldehyde) as prisms, m. p. 232—233° (Found: N, 23·1. $C_9H_{15}ON_3$ requires N, 23·2%). Light absorption (in chloroform): Maximum, 2740 A.; ε = 23,200. Inflexion, 2800 A.; ε = 21,700. When the semicarbazone was distilled in steam in the presence of oxalic acid 2-*methyl*cyclo*hex*-1-*enealdehyde* was obtained in quantitative yield, b. p. 103°/27 mm., n_{D}^{18} 1·5091 (Found: C, 77·3; H, 9·75. $C_8H_{12}O$ requires C, 77·35; H, 9·75%). Light absorption: Maxima 2420, 2510 A.; ε = 11,200 and 11,200 respectively. The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in red needles, m. p. 186—187° (capillary), 190—191° (Kofler block) (Found: N, 18·1. Calc. for $C_{14}H_{16}O_4N_4$: N, 18·4%). Light absorption (in chloroform): Maximum, 3870 A.; ε = 29,500. [Howton, *loc. cit.*, gives m. p. 192·4—192·7° (corr.). Rapson and Shuttleworth, *loc. cit.*, give b. p. 66—68°/10 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4898, for 6-methyl*cyclo*hex-1-enealdehyde (XI), m. p. 207—209° for its semicarbazone, and m. p. 179° for its 2 : 4-dinitrophenylhydrazone. Wallach and Isaac, *loc. cit.*, give m. p. 208—212° for the semicarbazone of an aldehyde, either (X) or (XI).]

2-*Methyl*cyclo*hex*-1-*enecarboxylic Acid*.—An alcoholic solution of the aldehyde (200 mg.) was heated for 30 minutes with aqueous silver nitrate to which an excess of sodium hydroxide solution had been added. The filtered solution was extracted with ether, acidified, and re-extracted. The latter extract yielded 2-methyl*cyclo*hex-1-enecarboxylic acid (125 mg.), m. p. 80—82°, raised to 86° on crystallisation from aqueous methanol (Perkin, *J.*, 1905, **87**, 1068, gives m. p. 87°; Mousseron *et al.*, *Compt. rend.*, 1946, **223**, 36, give m. p. 88°. Rapson and Shuttleworth, *loc. cit.*, give m. p. 105° for 6-methyl*cyclo*hex-1-enecarboxylic acid).

4-(2′-*Methyl*cyclo*hex*-1′-*enyl*)*but*-3-*en*-2-*one* (VII).—The unsaturated aldehyde (X) (3·0 g.) in acetone (5 c.c.) was added during 5 minutes to a stirred solution of sodium hydroxide (0·3 g.) in a mixture of acetone (40 c.c.) and water (15 c.c.) at 5°. The mixture was allowed to warm to room temperature during 30 minutes, and was then stirred for a further 1½ hours. Working up with ether as before gave 4-(2′-*methyl*cyclo*hex*-1′-*enyl*)-*but*-3-*en*-2-*one* (2·5 g.; 63%) as a pleasant-smelling liquid, b. p. 82—83°/0·2 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·5592 (Found: C, 80·0; H, 9·75. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). Light absorption: Maxima, 2200, 2960 A.; ε = 4,000 and 20,300 respectively. The *semicarbazone* crystallised from methoxyethanol in small plates, m. p. 242° (decomp.; m. p. depends on rate of heating) (Found: N, 19·2. $C_{12}H_{19}ON_3$ requires N, 19·0%). Light absorption (in chloroform): Maximum, 3030 A.; ε = 40,900. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in two forms, light red needles and dark red prisms, both with m. p. 194° (Found: N, 16·0. $C_{17}H_{20}O_4N_4$ requires N, 16·25%). Light absorption (in chloroform): Maximum, 4020 A.; ε = 39,900.

4-(6′-*Methyl*cyclo*hexa*-1′ : 3′-*dienyl*)*but*-3-*en*-2-one (XIV).—Dihydro-*o*-tolualdehyde (23 g.) in acetone (50 c.c.) was added to a stirred solution of sodium hydroxide (2·5 g.) in water (80 c.c.) and acetone (200 c.c.) at 0°. After being stirred for 30 minutes at this temperature, the mixture was allowed to warm to room temperature, and was then stirred for an hour. Isolation with ether gave the triply unsaturated *ketone* (15·2 g.) as a light yellow, pleasant-smelling liquid, b. p. 141°/22 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·5985 (Found: C, 80·9; H, 8·85. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%). Light absorption: Maxima, 2290, 3370 A.; ε = 6,000 and 17,500 respectively. The *semicarbazone* crystallised from methoxyethanol in light yellow plates, m. p. 205° (Found: N, 19·3. $C_{12}H_{17}ON_3$ requires N, 19·15%). Light absorption: Maxima 2550, 3190, 3340, and 3500 A.; ε = 13,200, 19,100, 25,000, and 20,200 respectively. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in very dark red needles, m. p. 170—171° (Found: N, 16·5. $C_{17}H_{18}O_4N_4$ requires N, 16·35%). Light absorption (in chloroform): Maximum 4120 A.; ε = 34,900.

4-(2′-*Methyl*cyclo*hexyl*)*butan*-2-*one* (XII).—(*a*) The triply unsaturated ketone (XIV) (3·24 g.) in ethyl acetate (40 c.c.) was shaken with hydrogen and platinic oxide until absorption was complete (1340 c.c. at 8°/756 mm., equivalent to 2·85 |=). The catalyst and solvent were removed, and distillation of the residue gave the saturated *ketone* (2·8 g.) as a mobile liquid, b. p. 115°/24 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4689 (Found: C, 78·3; H, 11·5. $C_{11}H_{20}O$ requires C, 78·5; H, 11·95%). The *semicarbazone* crystallised from methanol in plates, m. p. 173—174° (Found: N, 18·8. $C_{12}H_{23}ON_3$ requires N, 18·65%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol in small needles, m. p. 86° (Found: N, 15·8. $C_{17}H_{24}O_4N_4$ requires N, 16·1%).

(*b*) The doubly unsaturated ketone (VII) (187 mg.) in methanol (10 c.c.) was shaken in hydrogen and platinic oxide until absorption was complete (56 c.c. at 20°/765 mm., equivalent to 2·0 |=). The catalyst was filtered off, and the semicarbazone was made from half of the filtrate, and was obtained as plates, m. p. 175°, undepressed on admixture with the sample previously obtained. The 2 : 4-dinitrophenylhydrazone was made from the remaining solution, and formed needles, m. p. 84—85°, undepressed on admixture with the sample obtained previously.

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