433. *Studies in the Polyene Series. Part XXXIII. The Preparation of 6-Methylocta-3 : 5 : 7-trien-2-one, a Key Intermediate for the Synthesis of Vitamin A and its Analogues.*

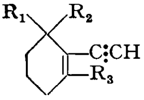
By G. W. H. Cheeseman, Sir Ian Heilbron, E. R. H. Jones, F. Sondheimer, and B. C. L. Weedon.

In the development of new approaches for the synthesis of vitamin A and its analogues, the key intermediate 6-methylocta-3 : 5 : 7-trien-2-one (II) has been prepared from readily available starting materials.

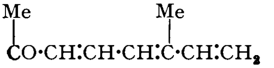
Condensation of crotonylideneacetone with acetylene gives the carbinol (VII) which, by partial hydrogenation and treatment of the resulting vinylcarbinol (VIII) with dilute acids, is isomerised to the triene carbinol (IX), Oppenauer oxidation of which yields the required ketone (II).

The diene carbinol (XIV) is obtained either by partial hydrogenation of (XII) and treatment of the divinyl carbinol (XIII) so formed with dilute acids, or alternatively by partial reduction of (XV). Oxidation of (XIV) with acetone and aluminium *tert.*-butoxide gives the ketone (II) directly.

Schemes for the synthesis of vitamin A and its analogues, which involve the condensation of ethynyl*cyclo*hexenes with unsaturated aldehydes and ketones and the anionotropic rearrangement of the resulting carbinols to the fully conjugated isomers, were outlined in Part XXV of this series (Heilbron, Jones, and Richardson, this vol., p. 287; cf. Heilbron, *J.*, 1948, 386). Subsequent papers (Heilbron, Jones, Weedon, *et al.*, this vol., pp. 742, 2023) have described progress made along these lines. In view of the general nature of the rearrangement (cf. Jones, *Ann. Reports*, 1944, **41**, 148), it was to be expected that primary alcohols of the type (IV; R_1, R_2, and R_3 = H or Me) could readily be prepared by condensation of the ethynyl*cyclo*hexenes (I; R_1, R_2, and R_3 = H or Me) with the hitherto unknown triene ketone (II) and rearrangement of the resulting tertiary carbinols (III; R_1, R_2, and R_3 = H or Me). It will be noted that these primary alcohols (IV) bear a close structural relation to vitamin A (V). The successful development of this synthetic scheme to give (IV; $R_1 = R_2 = R_3 =$ H) is reported in the following publication in this series. This paper records the synthesis of the key intermediate (II) from the readily available materials, crotonylideneacetone (VI) and methyl vinyl ketone.

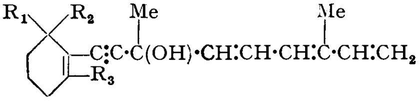


(I.)

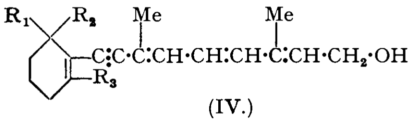


$$\overset{Me}{\underset{|}{C}}O\cdot CH{:}CH\cdot CH{:}\overset{Me}{\underset{|}{C}}\cdot CH{:}CH_2$$

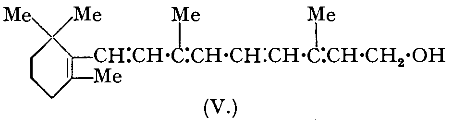
(II.)



(III.)



(IV.)

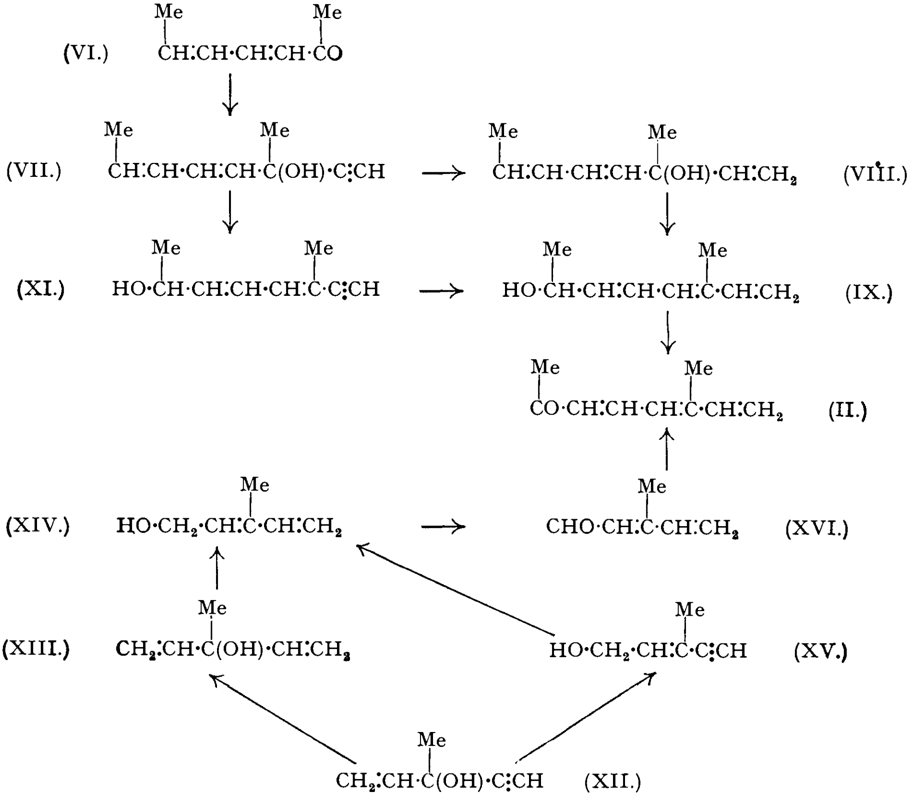


(V.)

The ethynylcarbinol (VII), possessing the complete C_9 skeleton of (II), was readily obtained by treatment of crotonylideneacetone (VI) with 2 moles of lithium acetylide in liquid ammonia. The crude product was shown, by light-absorption measurements, to contain *ca.* 20% of unchanged ketone; after removal of the latter by conversion into the semicarbazone, 3-*methylocta*-4 : 6-*dien*-1-*yn*-3-*ol* (VII), m. p. 19°, was obtained in an overall yield of 50%. With the exception of β-ionone (cf. Oroshnik, U.S.P. 2,425,201), this is believed to be the only case so far reported in which a conjugated diene ketone has been successfully converted into the corresponding ethynylcarbinol. When a large excess (4 mols.) of sodium acetylide (cf. Cymerman, Heilbron, and Jones, *J.*, 1945, 90) was used instead of lithium acetylide, extensive polymerisation occurred and the crude carbinol (VII) was isolated in only 25% yield.

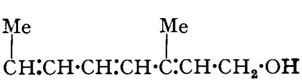
Hydrogenation of (VII) proceeded smoothly in the presence of a palladium–calcium carbonate catalyst and, by interrupting the reaction after 1 mole of hydrogen had been absorbed, the *vinylcarbinol* (VIII) was obtained in 95% yield (cf. Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84; Cymerman, Heilbron, and Jones, *loc. cit.*). This carbinol exhibited light-absorption properties typical of a diene chromophore and very similar to those of (VII), indicating that reduction of the latter had occurred exclusively at the acetylenic linkage (see Table).

When shaken with 0·05% sulphuric acid, the vinylcarbinol (VIII) was isomerised to the fully conjugated isomer, 6-*methylocta*-3 : 5 : 7-*trien*-2-*ol* (IX) (cf. *idem, loc. cit.*), the structure of which was established by complete hydrogenation and oxidation of the resulting saturated carbinol to the known 6-methyloctan-2-one (Heilbron, Jones, and Julia, this vol., p. 1430); no carboxylic acid was detected, as would have been the case had the rearrangement of (VIII) given any of the primary carbinol (X).



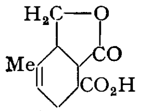
Oxidation of (IX) with acetone and aluminium *tert.*-butoxide or phenoxide yielded (65—80%) the required ketone, *6-methylocta-3 : 5 : 7-trien-2-one* (II) (*2 : 4-dinitrophenylhydrazone*; *semicarbazone*), with light-absorption properties similar to those of octatrienal. This ketone gave 6-methyloctan-2-one on hydrogenation.

The ethynylcarbinol (VII) underwent the expected anionotropic rearrangement when shaken with 1% sulphuric acid (cf. Heilbron, Jones, *et al.*, *J.*, 1943—1946) giving (90%) *6-methylocta-3 : 5-dien-7-yn-2-ol* (XI) from which the triene ketone (II), isolated as its 2 : 4-dinitrophenylhydrazone, was obtained by partial hydrogenation and oxidation of the resulting crude carbinol (IX). The structure of (XI) was confirmed by hydrogenation, followed by oxidation of the saturated product to 6-methyloctan-2-one.

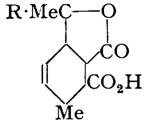


$\overset{\text{Me}}{\text{CH}}\text{:CH·CH:CH·}\overset{\text{Me}}{\text{C}}\text{:CH·CH}_2\text{·OH}$

(X.)



(XIX.)



(XX.)

The ketone (II) has also been synthesised from the acetylenic carbinol (XII), derived from methyl vinyl ketone (Cymerman, Heilbron, and Jones, *loc. cit.*), by the following routes. Partial hydrogenation of (XII) in the presence of a palladium–calcium carbonate catalyst yielded (60%) *3-methylpenta-1 : 4-dien-3-ol* (XIII), which when shaken with 1% sulphuric acid was converted into the conjugated *isomer* (XIV) in 25% yield. (XIV) was also obtained in 60% yield by partial hydrogenation of 3-methylpent-2-en-4-yn-1-ol (XV) (*idem, loc. cit.*). On oxidation of the diene carbinol (XIV) with acetone and aluminium *tert.*-butoxide, the initially formed aldehyde (XVI) condensed with excess of acetone, giving the ketone (II) directly in an overall yield of 30% (cf. Heilbron *et al.*, *J.*, 1938, 175). The postulated intermediate (XVI) in this reaction was also prepared by the method of Heilbron, Jones, Julia, and Weedon (*loc. cit.*) and shown to give the ketone (II) on condensation with acetone.

	$\lambda_{\mathrm{max.}}$, A.	$\varepsilon_{\mathrm{max.}}$
$\mathrm{CHMe{:}CH{\cdot}CH{:}CH{\cdot}CMe(OH){\cdot}C{\vdots}CH}$ (VII)	2270	26,500
$\mathrm{CHMe{:}CH{\cdot}CH{:}CH{\cdot}CMe(OH){\cdot}CH{:}CH_2}$ (VIII)	2290	27,500
$\mathrm{CH_2(OH){\cdot}CH{:}CMe{\cdot}CH{:}CH_2}$ (XIV)	2280	24,500
$\mathrm{CHMe(OH){\cdot}CH{:}CH{\cdot}CH{:}CH_2}$ [1]	2230	28,000
$\mathrm{CHMe(OH){\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}C{\vdots}CH}$ (XI)	2600	35,500
	2640 *	32,000
	2690 *	27,500
$\mathrm{CHMe(OH){\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CH{:}CH_2}$ (IX)	2590	32,500
	2670	40,500
	2770	32,500
$\mathrm{CHMe(OH){\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C{\vdots}CH}$ [2]	2600	34,000
	2470 *	24,500
	2730 *	24,500
$\mathrm{Me{\cdot}CO{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CH{:}CH_2}$ (II)	3080	31,500
$\mathrm{CHO{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CHMe}$ [3]	3060 †	41,000

* Inflexion. † In hexane.

[1] Heilbron, Jones, McCombie, and Weedon, *loc. cit.*

[2] Heilbron, Jones, and McCombie, *J.*, 1944, 134.

[3] Hausser, Smakula, Kuhn, and Hoffer, *Z. physikal. Chem.*, 1935, *B*, **29**, 371.

When treated with maleic anhydride, (XIV) behaved in the manner characteristic of conjugated dienols (Heilbron, Jones, McCombie, and Weedon, *loc. cit.*) and yielded the latonic *acid* (XIX). Similarly the *acids* (XX; $\mathrm{R = C{\vdots}CH}$) and (XX; $\mathrm{R = CH{:}CH_2}$) were obtained from the carbinols (VII) and (VIII), respectively.

The various compounds described in this paper all exhibited the expected light-absorption properties (see Table).

EXPERIMENTAL.

All the operations were performed in an atmosphere of nitrogen. Light-absorption data were determined in ethanol except where stated otherwise. Data for most of the compounds described below are given in the Table.

3-*Methylocta*-4 : 6-*dien*-1-*yn*-3-*ol* (VII).—Liquid ammonia (4 l.) was poured into a 10-l. flask, provided with a gas-inlet tube and a mechanical stirrer and cooled in a carbon dioxide–alcohol bath. A vigorous stream of acetylene (*ca.* 3 l./min.) was bubbled into the stirred liquid, and lithium (30 g.), cut into small pieces, was added during 15 minutes. A vigorous evolution of hydrogen was observed, which soon stopped, indicating complete conversion of the lithium into the acetylide which was obtained as a milky suspension. The acetylene flow was reduced (to *ca.* 200 c.c./min.) and crotonylideneacetone (200 g.; b. p. 86°/24 mm., n_{D}^{21} 1·5210) in dry ether (800 c.c.) was added during 4 hours. The cooled mixture was stirred for a further 14 hours, and ammonium chloride (300 g.) was then gradually added. The ammonia was evaporated on the steam-bath, water and ether were added to the residue, and the ethereal layer was separated, washed with water, and dried ($MgSO_4$). The ethereal extract was evaporated, and the residue distilled giving a colourless liquid (203 g.), b. p. 72—78°/1 mm., n_{D}^{22} 1·5077. Light absorption : Maxima, 2280, 2700 A.; $E_{1\,\mathrm{cm.}}^{1\%}$, 1900 and 400 respectively.

Semicarbazide hydrochloride (60 g.), dissolved in hot water (60 c.c.), was added to a solution of potassium acetate (70 g.) in methanol (300 c.c.). After the mixture had been cooled, the potassium chloride deposited was filtered off and the filtrate was added to the crude carbinol, described above, dissolved in methanol (500 c.c.). The solution was heated at 60° for a few minutes and set aside at room temperature overnight. The solution was then poured into water (2·5 l.) and light petroleum (800 c.c.; b. p. 40—60°), and the mixture shaken. This caused the precipitation of crotonylideneacetone semicarbazone which was filtered off. The aqueous layer was shaken with more light petroleum, and the combined petroleum extracts were dried ($MgSO_4$) and cooled to 0°, whereupon further crotonylideneacetone semicarbazone separated. The mixture of magnesium sulphate and semicarbazone was filtered off and washed with cooled light petroleum (b. p. 40—60°), and the filtrate evaporated. The residue was distilled giving 3-*methylocta*-4 : 6-*dien*-1-*yn*-3-*ol* (126 g.), b. p. 68°/0·5 mm., m. p. 19°, n_{D}^{22} 1·5021, which contained no trace of ketonic material (Found : C, 79·7; H, 9·05. $C_9H_{12}O$ requires C, 79·35; H, 8·9%). Light absorption : see Table.

The carbinol (0·4 g.) and maleic anhydride (0·4 g.) were heated in benzene (5 c.c.) and then kept at room temperature overnight. The precipitated solid was recrystallised from water giving 6-*methyl*-3-(1′-*hydroxy*-1′-*methylprop*-2′-*ynyl*)cyclo*hex*-4-*ene*-1 : 2-*dicarboxylic acid* 2→1′-*lactone* (XX; $\mathrm{R = CH{\vdots}C}$) (0·5 g.) as plates, m. p. 213—215° (Found : C, 66·85; H, 5·8. $C_{13}H_{14}O_4$ requires C, 66·65; H, 6·0%).

3-*Methylocta*-1 : 4 : 6-*trien*-3-*ol* (VIII).—The acetylenic carbinol (VII) (112 g.) in methyl acetate (400 c.c.) was shaken in hydrogen in the presence of a palladium–calcium carbonate catalyst (5 g.; 6% of Pd), with periodic cooling, until 20·2 l. of hydrogen had been absorbed at 22°/767 mm., equivalent to 1 molar proportion. Removal of the catalyst and solvent, followed by fractionation of the residue, gave 3-*methylocta*-1 : 4 : 6-*trien*-3-*ol* (106·5 g.), b. p. 65—67°/0·8 mm., n_D^{20} 1·4975 (Found : C, 78·1; H, 10·15. $C_9H_{14}O$ requires C, 78·2; H, 10·2%). Light absorption : see Table.

The carbinol (0·3 g.) and maleic anhydride (0·3 g.) were heated in benzene (3 c.c.) and then kept at room temperature overnight. The precipitated solid was crystallised from water giving 6-*methyl*-3-(1′-*hydroxy*-1′-*methylprop*-2′-*enyl*)-cyclo*hex*-4-*ene*-1 : 2-*dicarboxylic acid* 2→1′-*lactone* (XX; R = CH_2:CH) (0·3 g.) as plates, m. p. 192—193° (Found : C, 66·15; H, 6·85. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·85%).

6-*Methylocta*-3 : 5 : 7-*trien*-2-*ol* (IX).—The above carbinol (VIII) (105 g.) was shaken with dilute sulphuric acid (1·5 l.; 0·05% w/v) in the presence of a trace of quinol for 90 minutes. The product was extracted with ether, washed with sodium hydrogen carbonate solution and water, and the dried ($MgSO_4$) extract evaporated. Distillation of the residue gave 6-*methylocta*-3 : 5 - 7-*trien*-2-*ol* (63 g.; 60%), b. p. 86—88°/0·7 mm., n_D^{22} 1·5501—1·5562 (the product was collected in several fractions which showed only slight differences in light-absorption intensity). Light absorption : see Table. A large amount of a transparent polymer was also obtained. When stronger acid was employed, this polymer was the main product. In smaller-scale experiments in which a solution of the carbinol (VIII) (*ca.* 50 g.) in ether (*ca.* 100 c.c.) was shaken with dilute sulphuric acid (0·05% w/v) for 3 hours, the yield of the rearranged carbinol was increased to 75%.

6-*Methyloctan*-2-*one*.—The above rearranged carbinol (1·56 g.) in acetone (10 c.c.) was shaken in hydrogen in the presence of platinic oxide until absorption was complete (820 c.c. of hydrogen absorbed at 20°/761 mm., equivalent to 2·95 double bonds). The catalyst was filtered off, and a large excess of chromic acid in dilute sulphuric acid was added to the filtrate. The mixture was heated on the steam-bath for 15 minutes, and the product was isolated by means of ether in the usual manner. The neutral fraction yielded 6-methyloctan-2-one (1·2 g.), b. p. 87°/24 mm., n_D^{21} 1·4225 (Heilbron, Jones, and Julia, this vol., p. 1430, give b. p. 70°/10 mm., n_D^{18} 1·4250). The semicarbazone crystallised from aqueous methanol in plates, m. p. 128°, undepressed on admixture with an authentic specimen (*idem, loc. cit.*, give m. p. 131°). The 2 : 4-*dinitrophenylhydrazone* crystallised from aqueous methanol in orange plates, m. p. 61—62° (Found : N, 17·45. $C_{15}H_{22}O_4N_4$ requires N, 17·4%).

No trace of acidic material was obtained from the oxidation.

6-*Methylocta*-3 : 5-*dien*-7-*yn*-2-*ol* (XI).—A solution of 3-methylocta-4 : 6-dien-1-yn-3-ol (3·0 g.) and a trace of quinol in ether (20 c.c.) was shaken with dilute sulphuric acid (200 c.c.; 1% w/v) for 5 hours. Isolation of the product in the usual way gave the rearranged *carbinol* (2·75 g.), b. p. 63°/0·1 mm., n_D^{19} 1·5361 (Found : C, 79·5; H, 8·95. $C_9H_{12}O$ requires C, 79·4; H, 8·9%). Light absorption : see Table.

6-*Methyloctan*-2-*one*.—The above carbinol (2·2 g.) in acetone (20 c.c.) was shaken in hydrogen in the presence of platinic oxide until absorption was complete (1490 c.c. of hydrogen absorbed at 21°/770 mm., equivalent to 3·8 double bonds). The catalyst was removed and the saturated carbinol was oxidised with chromic acid, in the manner described above, giving 6-methyloctan-2-one (1·4 g.), b. p. 80°/20 mm., n_D^{21} 1·4220. The semicarbazone crystallised from aqueous methanol in plates, m. p. 126—128°, undepressed on admixture with an authentic specimen. The 2 : 4-dinitrophenylhydrazone crystallised from aqueous methanol in plates, m. p. 61—62°, undepressed on admixture with the specimen described above.

3-*Methylpenta*-1 : 4-*dien*-3-*ol* (XIII).—A solution of 3-methylpent-4-en-1-yn-3-ol (10 g.) (Cymerman, Heilbron, and Jones, *J.*, 1945, 90) in methanol (30 c.c.) was shaken in hydrogen in the presence of a palladium–charcoal catalyst (1 g.; 2% of Pd) until 2410 c.c. (20°/757 mm.) of gas had been absorbed (equivalent to 1 molar proportion). After removal of the catalyst, the methanol solution was diluted with water, and the product isolated with ether in the usual manner. Distillation gave 3-*methylpenta*-1 : 4-*dien*-3-*ol* (6 g.), b. p. 68—72°/120 mm., n_D^{20} 1·4400 (Found : C, 73·4; H, 10·2. $C_6H_{10}O$ requires C, 73·4; H, 10·25%).

3-*Methylpenta*-2 : 4-*dien*-1-*ol* (XIV).—(*a*) A mixture of the above carbinol (5·7 g.), dilute sulphuric acid (360 c.c.; 1% w/v), and a trace of quinol was shaken at 20° for 4 hours. Isolation of the product with ether and distillation gave 3-*methylpenta*-2 : 4-*dien*-1-*ol* (1·5 g.), b. p. 106°/80 mm., n_D^{19} 1·4942 (Found : C, 72·95; H, 10·6. $C_6H_{10}O$ requires C, 73·4; H, 10·25%). Light absorption : see Table.

A solution of the carbinol (0·5 g.) and maleic anhydride (0·5 g.) in benzene (5 c.c.) was allowed to stand at 20° overnight. The solid which separated was recrystallised from water, giving 4-*methyl*-3-*hydroxymethyl*cyclo*hex*-4-*ene*-1 : 2-*dicarboxylic acid* 2→ω-*lactone* (XIX) (0·5 g.) as needles, m. p. 182—183° (Found : C, 60·9; H, 6·1. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·15%).

(*b*) A solution of 3-methylpent-2-en-4-yn-1-ol (10 g.) (*idem, loc. cit.*) in methyl acetate (30 c.c.) was shaken in hydrogen in the presence of a palladium–calcium carbonate catalyst (1 g.; 6% of Pd) until 2509 c.c. of gas had been absorbed at 20°/760 mm., whereafter the reaction was interrupted. Removal of the catalyst and solvent, and distillation of the residue, gave 3-methylpenta-2 : 4-dien-1-ol (6 g.), b. p. 68—71°/15 mm., n_D^{20} 1·4840—1·4920 (the product was collected in several fractions which differed but slightly in their light-absorption intensities). The maleic anhydride adduct, prepared as described above, had m. p. 182—183°, undepressed on admixture with a specimen from (*a*).

6-*Methylocta*-3 : 5 : 7-*trien*-2-*one* (II).—(*a*) A mixture of 6-methylocta-3 : 5 : 7-trien-2-ol (45 g.), aluminium *tert.*-butoxide (140 g.), dry benzene (3 l.), and dry acetone (1·4 l.) was heated under reflux for 24 hours. Ice and dilute sulphuric acid (10% w/v) were added, and the benzene layer separated and washed with water, sodium hydrogen carbonate solution, and again with water. The dried ($MgSO_4$) benzene solution was evaporated under reduced pressure, the temperature being kept below 50°, and the residue distilled rapidly in small batches, giving 6-*methylocta*-3 : 5 : 7-*trien*-2-*one* (30 g.) as a pale yellow unstable liquid, b. p. 79—80°/0·9 mm., n_D^{25} 1·5796—1·5880 (Found: C, 79·05; H, 9·15. $C_9H_{12}O$ requires C, 79·35; H, 9·15%). Light absorption : Maximum, 3080 A.; ε, 30,000. Each batch was collected in several fractions which showed only slight differences in light-absorption intensity. (No trace of unchanged carbinol could be detected, but a considerable amount of a transparent polymer was also formed.) The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark red needles, m. p. 203° (Found : N, 18·0. $C_{15}H_{16}O_4N_4$ requires N, 17·7%). Light absorption in chloroform (main band only) : Maximum, 4000 A.; ε, 43,000. The *semicarbazone* crystallised from methanol in plates which decomposed when heated (Found: N, 21·65. $C_{10}H_{15}ON_3$ requires N, 21·75%). Light absorption: Maxima, 2800, 3160, and 3290 A.; ε, 27,000, 52,000, and 40,500, respectively.

In small-scale experiments, the ketone (II) was obtained in yields up to 80%.

(*b*) A solution of 6-methylocta-3 : 5 : 7-trien-2-ol (4 g.) and aluminium phenoxide (9 g.) in acetone (60 c.c.) and benzene (130 c.c.) was heated under reflux for 24 hours. After cooling, the solution was poured into dilute sulphuric acid (10% w/v), and the benzene layer was separated and washed with dilute sodium hydroxide solution (10% w/v) and water. The benzene solution was dried and evaporated under reduced pressure. Distillation of the residue gave 6-methylocta-3 : 5 : 7-trien-2-one (2·4 g.), b. p. 51°/0·1 mm., n_{D}^{19} 1·5893—1·5991. Light absorption: Maximum, 3080 A.; ε, 31,500. The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in dark red needles, m. p. 203°, undepressed on admixture with a specimen from (*a*).

(*c*) A solution of 3-methylpenta-2 : 4-dien-1-ol (9·2 g.) and aluminium *tert.*-butoxide (27 g.) in acetone (270 c.c.) and benzene (675 c.c.) was heated under reflux for 36 hours. Isolation of the product in the usual manner and distillation gave 6-methylocta-3 : 5 : 7-trien-2-one (3·8 g.), b. p. 49—54°/10^{-2} mm., n_{D}^{19} 1·5805—1·5890. Light absorption: Maximum, 3080 A.; ε, 30,000. The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in dark red needles, m. p. 204—205°, undepressed on admixture with a specimen from (*a*).

(*d*) A solution of 6-methylocta-3 : 5-dien-7-yn-2-ol (4·1 g.) in methyl acetate (30 c.c.) was shaken in an atmosphere of hydrogen in the presence of a palladium–calcium carbonate catalyst (0·4 g.; 0·3% of Pd) until 740 c.c. of hydrogen had been absorbed at 18°/754 mm., equivalent to 1 molar proportion. The reaction was interrupted and the catalyst and solvent were removed. Distillation of the residue gave the crude triene carbinol (2·9 g.), b. p. 60—65°/0·1 mm., n_{D}^{21} 1·5329—1·5469, which was dissolved in acetone (90 c.c.) and added to a solution of aluminium *tert.*-butoxide (9·0 g.) in benzene (200 c.c.). The solution was boiled under reflux for 24 hours, and the product isolated in the usual way, giving the crude ketone (1·7 g.), b. p. 52—55°/0·1 mm., n_{D}^{17} 1·5752—1·5792. Light absorption: Maximum, 3050 A.; $E^{1\%}_{1\,\mathrm{cm.}}$, 1840—2100. The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in dark red needles, m. p. 203°, undepressed on admixture with a specimen from (*a*).

(*e*) (With MARC JULIA.) A solution of 3-methylpenta-2 : 4-dien-1-al (1·35 g.; crude, b. p. 54—61°/20 mm., n_{D}^{22} 1·4883. Light absorption: Maxima, 2520 and 2590 A.; $E^{1\%}_{1\,\mathrm{cm.}}$, 1600 and 1580, respectively. Inflexion, 2420 A.; $E^{1\%}_{1\,\mathrm{cm.}}$, 1300), prepared from 1-ethoxy-3-methylpent-4-en-1-yn-3-ol (4·1 g.) by the method of Heilbron, Jones, Julia, and Weedon (*loc. cit.*), and aluminium *tert.*-butoxide (6 g.) in acetone (40 c.c.) and benzene (100 c.c.) was boiled under reflux for 12 hours. Isolation of the product in the usual manner gave an oil (0·5 g.), b. p. *ca.* 50°/10^{-2} mm., n_{D}^{18} 1·5561. Light absorption: Maximum, 3050 A., $E^{1\%}_{1\,\mathrm{cm.}}$, 1140, indicating a content of *ca.* 50% of the ketone (II). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark red needles, m. p. 174—176°, and is isomeric with the derivative described above (Found: C, 56·45; H, 5·4; N, 17·65. $C_{15}H_{16}O_4N_4$ requires C, 56·8; H, 5·1; N, 17·7%). Light absorption in chloroform (main band only): Maximum, 4050 A.; ε, 35,000.

The condensation was also effected by adding a solution of sodium hydroxide (0·6 g.) in aqueous alcohol (4 c.c.; 50% w/v) to a cooled solution of the crude aldehyde (1·8 g.) in acetone (8 c.c.). After 15 minutes at 20°, the resulting dark brown mixture was acidified with dilute sulphuric acid (10% w/v), and the crude ketone (1·5 g.), b. p. *ca.* 40°/10^{-3} mm., isolated in the usual way. Light absorption: Maximum, 3050 A.; $E^{1\%}_{1\,\mathrm{cm.}}$, 1000. The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in needles, m. p. 204°, undepressed on admixture with a specimen from (*a*).

6-*Methyloctan*-2-*one*.—A solution of 6-methylocta-3 : 5 : 7-trien-2-one (0·5 g.) in methyl acetate (10 c.c.) was shaken in hydrogen in the presence of platinic oxide until absorption was complete (250 c.c. of hydrogen absorbed at 13°/772 mm., equivalent to 2·9 double bonds). Removal of catalyst and solvent gave 6-methyloctan-2-one (0·45 g.), n_{D}^{18} 1·4225. The semicarbazone crystallised from aqueous methanol in plates, m. p. 128°, undepressed on admixture with the specimen described above.

The authors are indebted to the Rockefeller Foundation for financial assistance and to the Department of Scientific and Industrial Research for a Senior Award (to F. S.) and a Maintenance Grant (to G. W. H. C.). One of them (G. W. H. C.) thanks the University of London and the Clothworkers Company for a William Gilles Research Fellowship. Light absorption data were determined by Dr. E. A. Braude.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.7.

[*Received, March 7th,* 1949.]