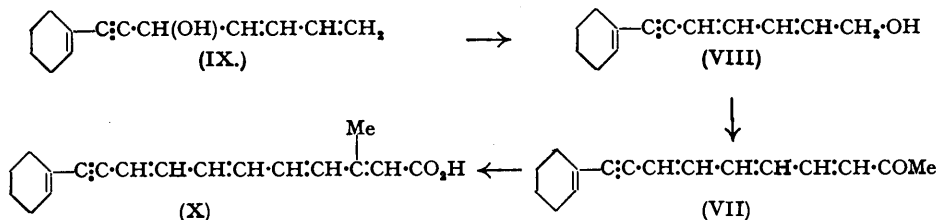




of the tertiary alcohol (V; R = H). Anionotropic rearrangement of the latter, by treatment with 1% sulphuric acid, yielded the impure isomer (II; R = H), which was isolated as an approximately 40% concentrate by chromatography, and was characterised by formation of the *p*-phenylazobenzoate, m. p. 114°. This concentrate polymerised rapidly, even at 0° in an inert atmosphere, and consequently further purification of the primary alcohol was not attempted and no significant biological assays were possible. The difference in stability of (II; R = H) and its C<sub>3</sub>-methyl homologue (II; R = Me) was very marked. Similar, though less pronounced, differences in stability have previously been observed between the methyl ether and the acetate of (I; R = H) and the corresponding derivatives of vitamin A (I; R = Me) (Cheeseman, Heilbron, Jones, Sondheimer, and Weedon, *J.*, 1949, 1516).

Oxidation of an αβ-unsaturated primary alcohol with aluminium *tert.*-butoxide and acetone to the corresponding aldehyde which, under the conditions of the reaction, condenses with excess of acetone yielding a polyene ketone, has been utilised on a number of occasions as a means of extending a polyene chain (see for example Schinz, Ruzicka, Seidel, and Tavel, *Helv. Chim. Acta*, 1947, 30, 1810; Cheeseman, Heilbron, Jones, Sondheimer, and Weedon, *J.*, 1949, 2031). As an alternative method for the synthesis of the ketone (VII), prepared earlier from (III) and octatrienal and isolated as the semicarbazone (Heilbron, Jones, Lewis, Richardson, and



Weedon, *J.*, 1949, 742), this process has been applied to the alcohol (VIII). The latter was obtained by reaction of the Grignard complex of (III) with penta-2:4-dien-1-al to give (IX) in 70% yield, and subsequent anionotropic rearrangement. Treatment of (VIII) with aluminium *tert.*-butoxide and acetone gave a crude product from which the ketone (VII) was isolated by use of the Girard T reagent (Girard and Sandulesco, *Helv. Chim. Acta*, 1936, 19, 1095) and chromatography of the ketonic fraction. The ketone was characterised by the formation of the semicarbazone and the 2:4-dinitrophenylhydrazone, the light-absorption properties of the former derivative being in good agreement with those reported earlier (Heilbron, Jones, Lewis, Richardson, and Weedon, *loc. cit.*).

When a 85% concentrate of (VII) was administered orally in arachis oil to rats fed on a diet deficient in vitamin A, in doses which would have revealed activity of the order of one thousandth of that of vitamin A, no growth responses were observed. The corresponding alcohol has previously been reported to be inactive (*idem, loc. cit.*).

A Reformatsky reaction of (VII) with methyl bromoacetate led to the isolation of a small amount of a crystalline acid which exhibited light-absorption properties in agreement with those expected for structure (X).

The light-absorption data of the majority of the compounds described in this paper are given in the table.

#### EXPERIMENTAL.

Light-absorption data were determined in ethanol except where otherwise stated.

All the operations were performed in an inert atmosphere.




2:4-Dinitrophenylhydrazones were purified by chromatographic adsorption on alumina from benzene solution. All other chromatograms were on alumina which had been partly deactivated as described by Cheeseman, Heilbron, Jones, and Weedon (*J.*, 1949, 3120).

Penta-2:4-dien-1-al was prepared according to Woods and Sanders (*J. Amer. Chem. Soc.*, 1947, 69, 2926) and exhibited a light-absorption maximum at 2580 Å ( $\epsilon = 29,000$ ). The 2:4-dinitrophenylhydrazone had m. p. 176—177° (*idem, loc. cit.*, give m. p. 176—177°); light absorption in chloroform (main band only): 3860 Å;  $\epsilon = 37,500$ .

8-cyclohex-1'-enyl-2:6-dimethylocta-1:3:5-trien-7-yn-1-carboxylic Acids (VI; R = H).—The method of preparation differs somewhat from that previously described (Heilbron, Jones, and Richardson, *J.*, 1949, 287).

A mixture of 8-cyclohex-1'-enyl-6-methylocta-3:5-dien-7-yn-2-one (9.9 g.) (*idem, loc. cit.*), ethyl bromoacetate (7.6 g.), benzene (80 c.c.), activated zinc wool (3.1 g.) (*cf. Fieser and Johnson, J. Amer. Chem. Soc.*, 1940, 62, 575), and a trace of iodine was heated under reflux for 45 minutes. The mixture was then cooled, decanted from a small amount of unreacted zinc, and shaken with 2*N*-acetic acid (*ca.*

250 c.c.). The benzene solution was washed with aqueous sodium hydrogen carbonate solution, dried, and evaporated under reduced pressure. The residual oil (11.5 g.),  $n_D^{20}$  1.5602, was dissolved in benzene (100 c.c.), toluene-*p*-sulphonic acid (42 mg.) was added, and the mixture was heated under reflux for 5 hours. The water which separated during the first 30 minutes was removed by azeotropic distillation.

	$\lambda_{\max.}, \text{\AA}$	$\epsilon_{\max.}$
Ketone (IV; R = H) .....	2910 *	32,000
	3000	36,500
Ketone (IV; R = Me) <sup>1</sup> .....	3080	31,500
	2280	19,500
Alcohol (V; R = H) .....	2650	38,500
	2730	36,500
	2280	18,500
	2600	27,500
Alcohol (V; R = Me) <sup>2</sup> .....	2700	38,000
	2800	31,500
	3230	59,000
<i>p</i> -Phenylazobenzoate of (II; R = H) † .....	3230	59,000
<i>p</i> -Phenylazobenzoate of (II; R = Me) <sup>2</sup> ‡ .....	3250	56,500
Alcohol (IX) .....	2270	32,000
 -C≡C-CMe(OH)·CH·CH·CH·CHMe <sup>3</sup> .....	2270	39,000
	2370	30,000
Alcohol (VIII), solid .....	2820 *	28,000
	2910	29,000
	3050 *	25,500
Alcohol (VIII), liquid .....	2820	24,500
	2910	25,500
	3040	21,500
	2910	21,500
 -C≡C-CMe·CH·CH·CH·CMe-OH <sup>3</sup> .....	3060	15,000
	2910	21,500
<i>p</i> -Phenylazobenzoate of (VIII) † .....	2680 *	17,000
	3080	40,500
	3290 *	19,000
Ketone (VII) .....	2630	9,500
	3500	35,500
	2450	18,000
 -C≡C-CMe·CH·CH·CH-COMe <sup>3</sup> .....	3350	23,000
	3600	38,500
Acid (X) .....	3600	38,500
Acid (VI; R = H), <sup>3</sup> m. p. 179° .....	2570	11,000
	2600	12,000
	3390	27,500
	3450	34,000
Ester (VI; R = Me) .....	3450	34,000

\* Inflexion.

† In hexane.

‡ In chloroform.

<sup>1</sup> Cheeseman, Heilbron, Jones, Sondheimer, and Weedon, *J.*, 1949, 2031.<sup>2</sup> Cheeseman, Heilbron, Jones, and Weedon, *J.*, 1949, 3120.<sup>3</sup> Heilbron, Jones, and Richardson, *J.*, 1949, 287.

The mixture was cooled, washed with aqueous sodium hydrogen carbonate, dried, and evaporated, giving the crude ester as a viscous oil (11.5 g.),  $n_D^{25}$  1.6200. This was dissolved in a solution of potassium hydroxide (30 g.) in methanol (300 c.c.), and the solution kept at 20° for 72 hours. Water (900 c.c.) was added, the non-hydrolysable material was extracted with ether, and the aqueous solution was then acidified (to pH 4) with phosphoric acid. The liberated acid was isolated with ether, and crystallised from the same solvent yielding acid "A" as pale yellow needles (2.1 g.), m. p. 179—180° (Heilbron, Jones, and Richardson, *loc. cit.*, give m. p. 179°). Evaporation of the ethereal mother liquors and crystallisation of the residue from aqueous methanol gave acid "B" as needles (1.68 g.), m. p. 151—152° (*idem, loc. cit.*, give m. p. 153°).

In another experiment, the crude dehydrated ester (6.0 g.),  $n_D^{25}$  1.6200, was dissolved in light petroleum (b. p. 40—60°; 25 c.c.), and the solution was poured on to a column of alumina (600 g.; grade IV). The chromatogram was developed first with the same solvent and then with a mixture (1 : 2) of benzene and light petroleum (b. p. 40—60°). The least strongly adsorbed band was eluted, giving an oil (3.7 g.),  $n_D^{28}$  1.6283. Distillation yielded *ethyl 8-cyclohex-1'-enyl-2 : 6-dimethylocta-1 : 3 : 5-trien-7-yne-1-carboxylate* (3.35 g.) as a mixture of geometrical isomers, b. p. 120° (bath temp.)/10<sup>-4</sup> mm.,  $n_D^{25}$  1.6470, which partially solidified when kept at 0° (Found : C, 80.1; H, 8.65. C<sub>18</sub>H<sub>24</sub>O<sub>2</sub> requires C, 80.25; H, 8.5%). Light absorption : see table.

9-cycloHex-1'-enyl-3 : 7-dimethylnona-2 : 4 : 6-trien-8-yn-1-ol (II; R = Me).—A solution of the acid "A" (380 mg.), m. p. 179°, in ether (25 c.c.) was cooled to 0° and treated with an ethereal solution of diazomethane (50% excess; standardised against benzoic acid). After the mixture had been kept at 0° for 5 minutes, it was warmed to 30° to expel the excess of diazomethane, and the solvent was then removed under reduced pressure giving the methyl ester as a viscous oil which solidified at 0° and exhibited a light-absorption maximum at 3400 Å;  $E_{1\text{cm}}^{1\%} = 1840$ .

A solution of the methyl ester in ether (10 c.c.) was added dropwise to a stirred ethereal solution of lithium aluminium hydride (1.69% wt./vol.; 4.6 c.c.) at -65°. The mixture was stirred for 75 minutes at -30°, the unreacted hydride was then decomposed by the addition of ethyl acetate (0.2 g.), and the alcohol liberated by the addition of saturated aqueous ammonium chloride (0.66 c.c.). The temperature of the mixture was allowed to rise to 20°, the mixture was then filtered and the solid washed well with ether. The combined ethereal solutions were evaporated under reduced pressure giving a yellow viscous oil,  $n_D^{25} 1.618$ . Light absorption: maxima 2560 and 3200 Å;  $E_{1\text{cm}}^{1\%} = 690$  and 1280, respectively; inflexion, 3380 Å;  $E_{1\text{cm}}^{1\%} = 1000$ .

The crude alcohol solidified on trituration with pentane (2 c.c.). Recrystallisation from the same solvent gave the alcohol (180 mg.) as needles, m. p. 75—76° (Cheeseman, Heilbron, Jones, and Weedon, *J.*, 1949, 3120, give m. p. 75—76°). The anthraquinone-2-carboxylate, prepared from the crude alcohol, crystallised from acetone in crimson plates, m. p. 154°, undepressed on admixture with an authentic specimen (*idem, loc. cit.*, give m. p. 154—156°).

Similar reduction of the isomeric mixture of ethyl esters (3.0 g.) described above gave a mixture of alcohols (2.45 g.),  $n_D^{25} 1.6232$ . Light absorption: maxima, 2500 and 3200 Å;  $E_{1\text{cm}}^{1\%} = 820$  and 1580, respectively. Inflexion, 2800;  $E_{1\text{cm}}^{1\%} 630$ . Attempts to isolate the crystalline alcohol by low-temperature crystallisation or by chromatography were unavailing. A portion (250 mg.) of the crude alcohols was converted into the anthraquinone-2-carboxylates, one of which was isolated as crimson plates (97 mg.), m. p. 154° undepressed on admixture with the derivative described above.

Treatment of the acid "B" (700 mg.), m. p. 151—152°, with diazomethane gave the crude methyl ester (700 mg.) as a pale yellow oil which exhibited a light-absorption maximum at 3480 Å;  $E_{1\text{cm}}^{1\%} = 1080$ . This on reduction with lithium aluminium hydride gave a pale yellow oil (620 mg.),  $n_D^{25} 1.6217$ , which had a light-absorption maximum at 3240 Å,  $E_{1\text{cm}}^{1\%} = 1150$ , indicating an appreciable content of the corresponding alcohol. Attempts to crystallise the latter and to prepare a crystalline derivative were unsuccessful.

Octa-3 : 5 : 7-trien-2-one (IV; R = H).—A mixture of penta-2 : 4-dien-1-al (6 g.), aluminium *tert.*-butoxide (18 g.), acetone (250 c.c.), and benzene (250 c.c.) was refluxed for 20 hours and then cooled and poured into dilute sulphuric acid (750 c.c.; 10% wt./vol.). The organic layer was washed free from acid, dried, and evaporated. Distillation of the residue gave the *ketone* (2.5—3.75 g.) as a yellow oil, b. p. 44—45°/0.05 mm.,  $n_D^{25} 1.587$ , which polymerised rapidly even at 0° (Found: C, 78.4; H, 8.6.  $C_8H_{10}O$  requires C, 78.65; H, 8.25%). Light absorption: see table. The *semicarbazone* (obtained in 70% yield) crystallised from aqueous methanol in pale yellow needles, m. p. 187° (decomp.) (Found: N, 23.8.  $C_8H_{11}ON_3$  requires N, 23.45%). Light absorption: maxima 2990, 3130, and 3250 Å;  $\epsilon = 53,500, 73,500, \text{ and } 69,000$ , respectively.

Hexyl Methyl Ketone.—A solution of octa-3 : 5 : 7-trien-2-one (1 g.) in methanol (100 c.c.) was shaken in hydrogen in the presence of platinum oxide (10 mg.) until absorption was complete (565 c.c., at 17°/765 mm.; equivalent to 2.9 double bonds). The catalyst and solvent were removed and the residue (0.9 g.)  $n_D^{20} 1.4170$ , was converted into the 2 : 4-dinitrophenylhydrazone which crystallised from alcohol in orange prisms, m. p. 57° undepressed on admixture with an authentic specimen of the derivative of hexyl methyl ketone (Allen, *J. Amer. Chem. Soc.*, 1930, 52, 2955, gives m. p. 58°).

1-cycloHex-1'-enyl-3-methylnona-4 : 6 : 8-trien-1-yn-3-ol (V; R = H).—1-Ethynylcyclohexene (7.6 g.) in ether (50 c.c.) was added during  $\frac{1}{2}$  hour to a solution of ethylmagnesium bromide (from 1.7 g. of magnesium) in ether (110 c.c.). The mixture was heated under reflux for 2 hours and then cooled to 5°. A solution of octa-3 : 5 : 7-trien-2-one (6.3 g.) in ether (80 c.c.) was added dropwise during 20 minutes and the mixture stirred vigorously at 25° for 1 hour. The Grignard complex was decomposed by the addition of ammonium chloride (13 g.) in water (40 c.c.), and the product isolated by means of ether giving the crude alcohol (12 g.),  $n_D^{25} 1.5405$ . Light absorption: maxima, 2300, 2650, 2730, and 2980 Å;  $E_{1\text{cm}}^{1\%} = 780, 1100, 750, \text{ and } 270$ , respectively, indicating a *ca.* 65% content of the alcohol. Distillation of a portion (0.6 g.) of the crude product gave 1-cyclohex-1'-enyl-3-methylnona-4 : 6 : 8-trien-1-yn-3-ol (0.2 g.) as a pale yellow oil, b. p. 80—85° (bath temp.)/10<sup>-5</sup> mm.,  $n_D^{25} 1.5788$  (Found: C, 83.9; H, 9.05.  $C_{16}H_{20}O$  requires C, 84.15; H, 8.85%). Light absorption: see table.

9-cycloHex-1'-enyl-7-methylnona-2 : 4 : 6-trien-8-yn-1-ol (II; R = H).—A solution of (V; R = H) (2 g.; crude) and a trace of quinol in ether (20 c.c.) was shaken with dilute sulphuric acid (100 c.c.; 1% wt./vol.) at 20° for 30 hours. The ethereal layer was then separated, washed free from acid, dried, and evaporated. The residual oil was extracted with light petroleum (b. p. 40—60°), and the extract concentrated under reduced pressure to a volume of 20 c.c. and then poured on to a column of partially deactivated alumina (80 g.; grade III—IV). The chromatogram was developed first with the same solvent and then with benzene. Elution of the most strongly adsorbed band with ether-methanol (10 : 1) and evaporation of the solvent under reduced pressure gave a yellow viscous oil (0.92 g.),  $n_D^{25} 1.5641$ . Light absorption: maxima, 2270, 3080, and 3150 Å;  $E_{1\text{cm}}^{1\%} = 600, 640, \text{ and } 620$ , respectively, indicating an appreciable content (*ca.* 40%) of the rearranged alcohol (II; R = H). The product polymerised rapidly even at 0°.

A portion (0.2 g.) of the crude alcohol was esterified with *p*-phenylazobenzoyl chloride by the method described by Isler, Huber, Ronco, and Kofler (*Helv. Chim. Acta*, 1947, 30, 1911). The crude ester was

purified by chromatographic adsorption on alumina (grade III—IV) and obtained as an oil which partly solidified when kept at  $-70^{\circ}$  in contact with *n*-hexane-ethyl methyl ketone (20 : 1). The solid (30 mg.) was separated and recrystallised from acetone giving the *p*-phenylazobenzoate (13 mg.) as hygroscopic, pale orange microprisms, m. p.  $114^{\circ}$  (Found : C, 79.8; H, 6.95.  $C_{29}H_{28}O_2N_2$  requires C, 79.8; H, 6.5%). Light absorption : see table.

1-cycloHex-1'-enylhepta-4 : 6-dien-1-yn-3-ol (IX).—A solution of penta-2 : 4-dien-1-al (14 g.) in ether (15 c.c.) was added during  $\frac{1}{2}$  hour with vigorous stirring to cyclohexenylacetylenylmagnesium bromide (from 5.0 g. of magnesium and 25.0 g. of ethynylcyclohexene) in ether (650 c.c.). After the mixture had been stirred for a further 2 hours at  $20^{\circ}$ , the Grignard complex was decomposed by the addition of ammonium chloride (50 g.) in water (2 l.). Isolation of the product by means of ether gave the alcohol (22.5 g.) as a pale yellow oil, b. p.  $90-95^{\circ}$  (bath temp.)/ $10^{-5}$  mm.,  $n_D^{20}$  1.5566 (Found : C, 82.8; H, 8.8.  $C_{13}H_{16}O$  requires C, 82.9; H, 8.55%). Light absorption : see table. The *α*-naphthylurethane crystallised from benzene-light petroleum (b. p.  $40-60^{\circ}$ ) in micro-prisms, m. p.  $191^{\circ}$  (Found : C, 80.5; H, 6.3.  $C_{24}H_{28}O_2N$  requires C, 80.65; H, 6.5%).

1-cycloHexylheptan-3-ol and 1-cycloHexylheptan-3-one.—The alcohol (IX) (2 g.) in methanol (50 c.c.) was shaken in hydrogen in the presence of a platonic oxide catalyst (10 mg.) until absorption was complete (1208 c.c. at  $22^{\circ}$ /769 mm.; equivalent to 4.8 double bonds). After removal of catalyst and solvent, distillation gave 1-cyclohexylheptan-3-ol (1.7 g.) as a viscous oil, b. p.  $87-88^{\circ}$ /0.3 mm.,  $n_D^{20}$  1.4682 (Found : C, 79.3; H, 13.15.  $C_{13}H_{26}O$  requires C, 78.8; H, 13.2%).

The alcohol (1.3 g.) was dissolved in glacial acetic acid (5 c.c.) and a solution of chromium trioxide (0.5 g.) in water (1 c.c.) and acetic acid (4 c.c.) was added dropwise. The mixture was kept at  $20^{\circ}$  for 15 hours and then diluted with water (15 c.c.). The product was isolated with ether and distilled giving 1-cyclohexylheptan-3-one (1.2 g.), b. p.  $110^{\circ}$ /17 mm.,  $n_D^{20}$  1.4600 (Found : C, 79.0; H, 12.65.  $C_{13}H_{24}O$  requires C, 79.5; H, 12.3%). The 2 : 4-dinitrophenylhydrazone crystallised from alcohol in yellow needles, m. p.  $97-98^{\circ}$  (Found : N, 14.95.  $C_{15}H_{28}O_4N_4$  requires N, 14.9%).

7-cycloHex-1'-enylhepta-2 : 4-dien-6-yn-1-ol (VIII).—A solution of (IX) (27.5 g.) in ether (150 c.c.) was shaken with dilute sulphuric acid (600 c.c.; 10% wt./vol.) and a trace of quinol for 24 hours. The ethereal solution was separated, washed with sodium hydrogen carbonate solution and water, and dried, and the solvent evaporated. The residue was extracted with light petroleum (500 c.c.; b. p.  $40-60^{\circ}$ ), and the solution was filtered and the solvent evaporated yielding the crude re-arranged alcohol as a viscous oil (23 g.) which partly solidified on storage. Light absorption : maxima, 2290, 2800, and 2900 Å;  $E_{1\text{cm.}}^{1\%}$  = 560, 920, and 920, respectively. Inflexion, 3000 Å;  $E_{1\text{cm.}}^{1\%}$  = 730.

A portion (0.4 g.) of the crude alcohol was esterified with *p*-phenylazobenzoyl chloride (0.4 g.), by the method described by Isler, Huber, Ronco, and Kofler (*loc. cit.*), and the resulting ester was purified by chromatographic adsorption on alumina from a solution in light petroleum (b. p.  $40-60^{\circ}$ ). The crude product (190 mg.) was recrystallised from acetone giving the *p*-phenylazobenzoate (150 mg.) as orange micro-prisms, m. p.  $88^{\circ}$  (Found : C, 78.45; H, 6.5.  $C_{26}H_{24}O_2N_2$  requires C, 78.75; H, 6.1%). Light absorption : see table.

A solution of the crude alcohol (2 g.) in light petroleum (20 c.c.; b. p.  $40-60^{\circ}$ ) was poured on to a column of partially deactivated alumina (50 g.; grade III), and the chromatogram developed with the same solvent (100 c.c.). The column was divided mechanically and elution of the two main bands with ether and methanol gave : (i) An oil (0.45 g.). Light absorption : maxima, 2280, 2800, and 2910 Å;  $E_{1\text{cm.}}^{1\%}$  = 590, 1210, and 1540, respectively. Inflexion, 2650 Å;  $E_{1\text{cm.}}^{1\%}$  = 810. A portion (0.2 g.) was distilled, giving 7-cyclohex-1'-enylhepta-2 : 4-dien-6-yn-1-ol (0.1 g.) as a pale yellow viscous oil, b. p.  $90^{\circ}$  (bath temp.)/ $10^{-5}$  mm.,  $n_D^{20}$  1.6216 (Found : C, 82.9; H, 8.8.  $C_{13}H_{16}O$  requires C, 82.9; H, 8.55%). Light absorption : see table. When kept at  $0^{\circ}$ , the alcohol solidified and was recrystallised from hexane giving pale yellow needles, m. p.  $47-48^{\circ}$ .

(ii) An oil (0.4 g.). Light absorption : maxima, 2280, 2800, 2940, and 3000 Å;  $E_{1\text{cm.}}^{1\%}$  = 600, 1110, 1230, and 1120, respectively. Distillation of a portion (0.3 g.) gave an isomer (0.11 g.) of the alcohol as a pale yellow viscous oil, b. p.  $90^{\circ}$  (bath temp.)/ $10^{-3}$  mm.,  $n_D^{20}$  1.6130 (Found : C, 82.5; H, 8.9.  $C_{13}H_{16}O$  requires C, 82.9; H, 8.55%). Light absorption : see table.

10-cycloHex-1'-enyldeca-3 : 5 : 7-trien-9-yn-2-one (VII).—A mixture of the alcohol (VIII) (13.7 g., crude), aluminium *tert*-butoxide (18 g.), acetone (250 c.c.), and benzene (250 c.c.) was heated under reflux for 34 hours, cooled, and then poured into dilute sulphuric acid (750 c.c.; 10% wt./vol.). The organic layer was separated and the aqueous solution was extracted with ether. The combined ethereal extracts and benzene layer were washed with sodium hydrogen carbonate solution and water and dried. Evaporation of the solvents, finally at  $50^{\circ}$ / $10^{-3}$  mm., gave a viscous oil (15.1 g.),  $n_D^{20}$  1.6105. Light absorption : maxima, 2280, 2800—2900, and 3480—3650 Å;  $E_{1\text{cm.}}^{1\%}$  = 625, 475, and 380, respectively. Inflexions, 2400 and 3080 Å;  $E_{1\text{cm.}}^{1\%}$  = 430 and 350, respectively. The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate as dark red needles, m. p.  $181^{\circ}$  (decomp.) (sinters at  $176^{\circ}$ ) (Found : N, 13.45.  $C_{22}H_{22}O_4N_4$  requires N, 13.8%). Light absorption in chloroform (main band only) : maximum, 4150 Å;  $\epsilon$  = 51,000. An isomeric derivative was obtained from a specimen of the ketone made according to Heilbron, Jones, Lewis, Richardson, and Weedon (*J.*, 1949, 742) and crystallised from ethyl acetate-ethanol in dark red plates, m. p.  $183^{\circ}$  (decomp.) (Found : N, 13.75.  $C_{22}H_{22}O_4N_4$  requires N, 13.8%). Light absorption in chloroform (main band only) : maximum, 4210 Å;  $\epsilon$  = 46,500.

The crude ketone (5 g.) in alcohol (50 c.c.) was added to a solution of Girard reagent  $\tau$  (5 g.) (Girard and Sandulesco, *Helv. Chim. Acta*, 1936, 19, 1095) in glacial acetic acid (5 c.c.), and the mixture heated under reflux for 1 hour. The mixture was cooled and poured into ice and water containing sodium hydrogen carbonate (7.35 g.). The non-ketonic fraction was extracted with ether. The aqueous

solution was acidified by the addition of sulphuric acid (110 c.c.; 50% wt./vol.) and set aside at 20° for 1 hour. Isolation with ether gave the crude ketone (1.75 g.) as a dark brown oil,  $n_D^{21}$  1.622. Light absorption: maxima, 2280, 2640, and 3480 Å;  $E_{1\text{cm}}^{1\%} = 420, 375, \text{ and } 900$ , respectively. A solution of the crude ketone in light petroleum (10 c.c.; b. p. 40–60°) and benzene (3 c.c.) was poured on to a column of alumina (35 g.; grade II–III), and the chromatogram developed with a mixture of the same solvents (150 c.c.). The least strongly adsorbed band was eluted with acetone, giving a dark brown oil (1.1 g.),  $n_D^{22}$  1.6735. Light absorption: maxima, 2630 and 3510 Å;  $E_{1\text{cm}}^{1\%} = 420 \text{ and } 1250$ , respectively, indicating an approximately 80% content of the ketone. Distillation of a portion of this material (0.2 g.) gave 10-cyclohex-1'-enyldeca-3:5:7-trien-9-yn-2-one (0.13 g.) as a viscous orange oil, b. p. 130° (bath temp.)/ $5 \times 10^{-4}$  mm.,  $n_D^{19}$  1.687 (Found: C, 84.95; H, 8.3.  $C_{16}H_{18}O$  requires C, 84.9; H, 8.0%). Light absorption: see table. This ketone underwent no deterioration when kept at 0° for 2 weeks. The semicarbazone crystallised from methanol in yellow needles, m. p. ca. 198° (decomp.) (m. p. varied with the rate of heating). Light absorption in chloroform: maxima, 2650 and 3650 Å;  $\epsilon = 9000$  and 55,500, respectively. Inflexions, 3500 and 3800 Å;  $\epsilon = 36,000$  and 43,500, respectively [*idem, loc. cit.*, give m. p. 203° (decomp.)]. Light absorption in chloroform: maxima, 2650, 3640, and 3780 Å;  $\epsilon = 8500, 59,500, \text{ and } 46,500$ ].

10-cyclohex-1'-enyl-2-methyldeca-1:3:5:7-tetraen-9-yne-1-carboxylic Acid (X) (with D. G. LEWIS).—A mixture of the ketone (VII) (2.6 g.; crude) (Light absorption: maximum, 3500 Å;  $E_{1\text{cm}}^{1\%} = 1100$ ), methyl bromoacetate (3.6 g.), benzene (50 c.c.), activated zinc turnings (1.8 g.), and mercuric chloride (0.05 g.) was heated under reflux with stirring for 45 minutes. The mixture was cooled and the benzene solution was then decanted from the small amount of unreacted zinc and shaken with dilute acetic acid (150 c.c.; 5% wt./vol.). The benzene layer was separated, washed free from acid, dried, and evaporated giving the crude hydroxy-ester as an orange-red oil (3.0 g.) which was heated with anhydrous oxalic acid (10 g.) for 2 hours at 100°/0.1 mm. The mixture was cooled and then extracted with light petroleum (b. p. 40–60°). The extract was washed free from acid, dried, and evaporated yielding the crude dehydrated ester as a viscous orange oil (1.7 g.). Light absorption: maxima, 2800, 3050, 3500, and 3670 Å;  $E_{1\text{cm}}^{1\%} = 530, 430, 490, \text{ and } 550$ , respectively. Inflexions, 2530 and 2620 Å;  $E_{1\text{cm}}^{1\%} = 350 \text{ and } 400$ , respectively.

The crude ester was hydrolysed by treatment with a 10% solution of potassium hydroxide in methanol for 48 hours at 20°. Isolation of the acidic product gave an orange gum (0.64 g.). Light absorption: maxima, 2280, 2820, 2910, and 3560 Å;  $E_{1\text{cm}}^{1\%} = 520, 350, 350, \text{ and } 370$ , respectively. Methanol (5 c.c.) was added to the gum, and the mixture kept at 0° for 3 days during which time a small amount of solid was deposited. Recrystallisation of the latter from methanol yielded the acid as yellow prisms (20 mg.), m. p. 210–215° (decomp.) (Found: C, 80.4; H, 8.7.  $C_{16}H_{18}O_2$  requires C, 80.6; H, 7.5%). Light absorption: see table.

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

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