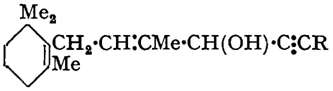
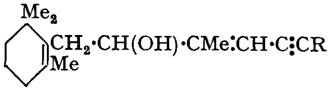
98. Studies in the Polyene Series. Part XXIII. Condensation of the C_{14}-Aldehyde [3-(2′ : 6′ : 6′-Trimethylcyclohexenyl)-1-methylcrotonaldehyde] with 1-Hexyne and 2-Methoxyhex-3-en-5-yne.

By J. Cymerman, Sir Ian Heilbron, E. R. H. Jones, and R. N. Lacey.

Condensations between the C_{14}-aldehyde (III) and both 1-hexyne (C_4H_9·C⋮CH) and 2-methoxyhex-3-en-5-yne [CH⋮C·CH:CH·CH(OMe)Me] can be effected in good yields. The resulting carbinols [I; R = C_4H_9 and CH:CH·CH(OMe)Me respectively] are rearranged (to II) in the expected manner with acids, but on elimination of

(I.)



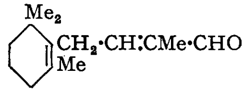


(II.)

water from (II), by treating the corresponding chloro-compounds with diethylaniline, the anticipated fully conjugated polyenynes are not formed. Since *iso*geronic acid is produced in each case on ozonolysis of the final products, it must be concluded that the failure to obtain conjugated systems of the vitamin A type is due to migration of the ring double bond into the α-position (*i.e.*, corresponding to that in α-ionone) at some undetermined stage in the syntheses.

In Part V of this series (Heilbron, Johnson, Jones, and Spinks, *J.*, 1942, 727) a scheme for the synthesis of polyene compounds related to vitamin A was propounded, one variant of which involved the condensation of the C_{14} aldehyde (III), derived from β-ionone, with conjugated acetylenylvinylcarbinols such as (IV). Experiments along these lines have now been carried out, and this paper contains an account of condensations with the readily available 1-hexyne and 2-methoxyhex-3-en-5-yne (Heilbron, Jones, and Weedon, *J.*, 1945, 82).

(III.)

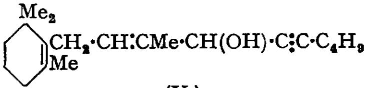


HC⋮C·CMe:CH·CH_2·OH (IV.)

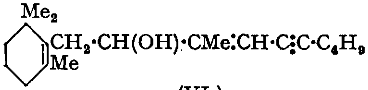
It was early appreciated that, as in all similar investigations in this series, reliable and significant results could only be expected by employing aldehyde of indubitable purity, regenerated from a pure crystalline derivative, as the starting material. Hydrolysis of the previously described thiosemicarbazone, even with 35% sulphuric acid and light petroleum (b. p. 100—120°), was effected only with difficulty and in very poor yield. Although we had hitherto failed to prepare a semicarbazone of the aldehyde, this proved possible with the material regenerated from the thiosemicarbazone. Subsequently, carefully fractionated aldehyde also yielded the *semicarbazone*, m. p. 148—150°, when the preparation was seeded. The light absorption properties of this derivative were in accord with those usually exhibited by the semicarbazones of αβ-unsaturated aldehydes (cf. Evans and Gillam, *J.*, 1943, 565). Refluxing the semicarbazone with 15% sulphuric acid and light petroleum (b. p. 80—100°) sufficed to regenerate the pure aldehyde in 90% yield.

[It may be noted here that the crystalline acid (obtained from pure β-ionone) gave only a poor yield of a very inhomogeneous aldehyde, possibly due to the difficulty of ensuring sufficient contact between the acid and the copper bronze during decarboxylation.]

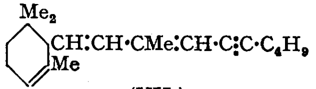
Condensation of the pure aldehyde (III) and 1-hexyne gave a 90% yield of the *carbinol* (V), giving a Zerewitinoff value of one and, as expected, showing no appreciable absorption in the usual ultraviolet region.



(V.)



(VI.)



(VII.)

Owing to its insolubility, no anionotropic rearrangement (Jones and McCombie, *J.*, 1943, 261 and following papers in this series) was observed on shaking with dilute sulphuric acid, but in aqueous alcoholic solution, 1% sulphuric acid was sufficient to give the rearranged *carbinol* (VI), the conjugated vinylacetylene system of which absorbed strongly at 2290 A.

A variety of methods was examined in attempts to dehydrate (VI) to the conjugated trienyne, including heating with potassium hydrogen sulphate and with *p*-toluenesulphonic acid in dioxan, pyrolysis of the *benzoate*, and treatment of the latter with dimethylaniline, but none gave satisfactory results. Either the carbinol was recovered unchanged or the product exhibited abnormal ultraviolet absorption. Accordingly the *chloro-compound* corresponding to (VI) was prepared by shaking an ethereal solution of the carbinol (V) with concentrated hydrochloric acid (cf. Heilbron, Jones, Lacey, McCombie, and Raphael, *J.*, 1945, 77). Treatment of this chloro-compound with diethylaniline at 150—160° yielded a *hydrocarbon*, $C_{20}H_{30}$, which absorbed five mols. of hydrogen on quantitative hydrogenation. The light absorption data for this compound, compared in Table I with those of somewhat related carbinols, etc., were at first not readily interpretable, but it was abundantly clear that the required fully conjugated trienyne, which would be expected to show maximal absorption at about 3000—3100 A., had not been produced. Indubitable evidence for the presence of the conjugated dienyne hydrocarbon (VII) in this product was provided by the isolation of *iso*geronic acid on

TABLE I.

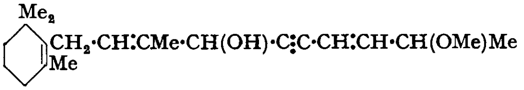
	$\lambda_{\text{max.}}$, A.	$\varepsilon_{\text{max.}}$.		$\lambda_{\text{max.}}$, A.	$\varepsilon_{\text{max.}}$.
Hydrocarbon (VII) (cf. (IX) in Table II)	2200	6,000	Deca-2 : 4 : 6 : 8-tetraen-1-ol [3]	2985	64,000
	2820	19,500		3110	64,000
	2900	19,500	Deca-2 : 4 : 6 : 8-tetraene [4]	2720	17,000
Deca-3 : 7-dien-5-yn-2 : 9-diol [1]	2650	21,500		2840	40,500
	2800	19,000		2960	58,500
Deca-3 : 5 : 7-trien-1-yn-9-ol [2]	2790	40,000		3200	58,500
	2920	60,000			
	3050	54,000			

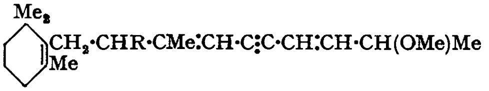
[1] Heilbron, Jones, and Raphael, *J.*, 1943, 268.
[2] Heilbron, Jones, and McCombie, *J.*, 1944, 134.
[3] Reichstein and Trivelli, *Helv. Chim. Acta*, 1932, **15**, 1074.
[4] Kuhn, *Angew. Chem.*, 1937, **50**, 705.

ozonolysis. The low yield of the latter (*ca.* 7%) does not compare unfavourably with that obtained from α-ionone itself (Lindenbaum, Andrews, and Young, *J. Amer. Chem. Soc.*, 1944, **66**, 2130) but it may indicate the presence of isomeric hydrocarbons.

Simultaneously with the investigations described above, the condensation of the C_{14} aldehyde (III) with 2-methoxyhex-3-en-5-yne was studied. The *methoxy-carbinol* (VIII), produced in excellent yield and showing light absorption corresponding to its conjugated vinylacetylene system, was smoothly isomerised in aqueous acetone containing 1% sulphuric acid to the rearranged *methoxy-carbinol* (IX; R = OH). Treatment of the parent compound (VIII) with concentrated hydrochloric acid similarly afforded the *chloro-compound* (IX; R = Cl). The structures of these two compounds (*i.e.*, IX; R = OH and Cl) follow from the methods of preparation, which have been investigated in detail in many analogous cases (see previous papers in this series), and their light absorption properties are practically identical (Table II). The maximal absorption is at somewhat longer wavelengths (*ca.* 150 A.) than has been observed with other conjugated dienyne systems, but these effects must obviously be attributed to the influence of substituent groups. It will be noted that this absorption is almost the same as that of the hydrocarbon (VII) (Table I) referred to above, thus providing additional evidence for the structure assigned to it. The carbinol (IX; R = OH) could not readily be dehydrated; it was recovered unchanged even after distillation at 220°/0·05 mm.

(VIII.)





(IX.)

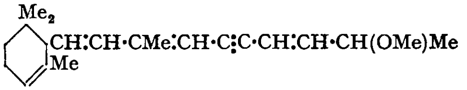
TABLE II.

	$\lambda_{\text{max.}}$, A.	$\varepsilon_{\text{max.}}$.		$\lambda_{\text{max.}}$, A.	$\varepsilon_{\text{max.}}$.
Methoxy-carbinol (IX; R = OH)	2710	20,500	Methoxy-compound (X) (cf. Table I)	3160	29,000
	2780 *	20,000		3100 *	28,000
	2880 *	16,000	Vitamin A [1]	3280	51,000
Chloro-compound (IX; R = Cl)	2800	19,000	Methyl ether [2]	3150	33,750
	2900	17,500			

* Inflexion.

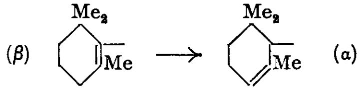
[1] Baxter and Robeson, *J. Amer. Chem. Soc.*, 1942, **64**, 2411.
[2] Oroshnik, *ibid.*, 1945, **67**, 1627.

Treatment of the chloro-compound with diethylaniline at 115° was only partially effective in splitting out hydrogen chloride, but at 160° this process was complete. The resulting methyl ether proved to be highly unstable, distilling as a pale yellowish oil but becoming red extremely rapidly on exposure to air. Its light absorption data (Table II) and the isolation of *iso*geronic acid on ozonolysis indicated that once again the expected fully conjugated system had not been obtained and the final product can only be formulated as (X).



(X.)

The explanation of this failure of the cyclic ethenoid linkage to participate in the conjugated system, as in the two examples quoted in this paper and as suggested in related earlier work (Heilbron, Jones, and Lacey, this vol., p. 27) is not clear. It has not been possible rigidly to prove that the original C_{14}-aldehyde actually contains a double bond in the β-ionone position, but the fact that a totally different isomeric aldehyde is produced when the synthesis is carried out with α-ionone must surely be regarded as strong indirect evidence. No isomerisation from the β- into the α-position, *i.e.*, would be expected to occur during the Grignard condensation involved in the preparation of either (V) or (VIII), but the same cannot be said either of the hydrochloric acid treatment employed to prepare the rearranged chloro-compound in each case, or of the subsequent dehydrochlorination stage with diethylaniline.



Oroshnik (*J. Amer. Chem. Soc.*, 1945, **67**, 1627) has recently claimed to have synthesised vitamin A methyl ether by the condensation of the ethynylcarbinol from β-ionone with 1-chloro-4-methoxy-2-methylbut-2-ene ($CH_2Cl\cdot CMe{:}CH\cdot CH_2\cdot OMe$), followed by semihydrogenation of the acetylenic bond, anionotropic rearrangement, and dehydration. It appears to us highly improbable that certain stages in the synthesis have proceeded in the manner claimed, and it may be noted that the final product, said to be vitamin A methyl ether, shows maximal absorption at 3150 A. This corresponds very closely to the absorption of the methyl ether (X) described above and it seems unlikely that the vitamin A chromophoric system is present in the final product. Had the author been able to provide evidence of the production of geronic acid on ozonolysis of the latter the claim might have been irrefutable, but since this is not the case, it can only be accepted with considerable reservations.

EXPERIMENTAL.

(Absorption spectra were determined in alcoholic solutions.)

3-(2′ : 6′ : 6′-*Trimethyl*cyclo*hexenyl*)-1-*methylcrotonaldehyde* (III).—Employing the method of Heilbron, Johnson, Jones, and Spinks (*J.*, 1942, 732) the action of sodium methoxide on a mixture of β-ionone (commercial, $n_{\mathrm{D}}^{16^\circ}$ 1·5156. Light absorption : Maxima, 2260 A., ε = 11,000; 2920 A., ε = 6,500) and ethyl chloroacetate in dry ether at − 60° gave the glycide ester (b. p. 110—130°/0·1 mm.) and then the glycide acid as a viscous reddish oil. The slow decarboxylation of the latter in the manner described (*loc. cit.*) yielded the aldehyde, b. p. 90—120°/0·01 mm., in 20% overall yield (calculated on β-ionone). Redistillation gave a pale yellowish oil, b. p. 105—106°/0·03 mm., 89—90°/0·01 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·5118.

The redistilled aldehyde was treated with semicarbazide acetate in the normal manner, giving the *semicarbazone* which separated from aqueous methyl alcohol as plates, m. p. 148—150° (Found : N, 16·05. $C_{15}H_{25}ON_3$ requires N, 15·9%). Light absorption : Maxima, 2220 A., ε = 7,500; 2650 A., ε = 30,000.

The powdered semicarbazone (15 g., m. p. 147°) was stirred and refluxed with sulphuric acid (200 c.c., 15% w/v) in the presence of light petroleum (80 c.c., b. p. 80—100°) in nitrogen until two clear layers were obtained (4—5 hours). The aqueous portion was extracted with light petroleum and the combined petroleum layers washed and dried. Removal of solvent under reduced pressure in an atmosphere of nitrogen gave the aldehyde (11 g., 92%), b. p. 50° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{19^\circ}$ 1·5109, $n_{\mathrm{D}}^{25^\circ}$ 1·5094.

1-(2′ : 6′ : 6′-*Trimethyl*cyclo*hexenyl*)-3-*methyldec-2-en-5-yn-4-ol* (V).—To an ice-cold solution of hexynylmagnesium bromide (Cymerman, Heilbron, and Jones, *J.*, 1944, 146) prepared from 1-hexyne (5 g.) and ethylmagnesium bromide (from 1 g. of magnesium) in dry ether (150 c.c.) a solution of the β-ionone C_{14} aldehyde (3·5 g., $n_{\mathrm{D}}^{25^\circ}$ 1·5094, regenerated from the semicarbazone) in dry ether (50 c.c.) was added with stirring during 20 minutes. The mixture was stirred at 20° for 19 hours and then refluxed for a further 6 hours. Decomposition of the Grignard complex with saturated ammonium chloride solution and isolation of the product with ether gave the *carbinol* (4·5 g., 92%) as a colourless slightly viscous oil, b. p. 80—85° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{21^\circ}$ 1·5064 (Found : C, 83·6; H, 11·3. $C_{20}H_{32}O$ requires C, 83·3; H, 11·2%). Active hydrogen (Zerewitinoff) : The carbinol (323 mg.) gave 25·2 c.c. of methane at 18°/763 mm. (0·95 active hydrogen atom per mol.). Light absorption : End absorption only, 2160 A., ε = 4,500. The carbinol failed to yield a solid derivative with α-naphthyl *iso*cyanate. The carbinol (0·5 g.) was heated with acetic anhydride (0·5 g.) and anhydrous potassium acetate at 120° for 1 hour in nitrogen. Water was added to the product which was neutralised with sodium bicarbonate. Isolation with ether gave the *acetyl* derivative as a pale yellow oil, b. p. 90° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4986 (Found : C, 79·8; H, 10·3. $C_{22}H_{34}O_2$ requires C, 79·95; H, 10·35%). Light absorption : End absorption only, 2200 A., ε = 5,000.

1-(2′ : 6′ : 6′-*Trimethyl*cyclo*hexenyl*)-3-*methyldec-3-en-5-yn-2-ol* (VI).—The above carbinol (5 g., $n_{\mathrm{D}}^{18^\circ}$ 1·5075) was dissolved in 80% aqueous alcohol containing 1% (w/v) of sulphuric acid, and the mixture was kept for 48 hours at 20°. The solution was poured into water and the product extracted with ether. Evaporation of the washed and dried extracts gave 1-(2′ : 6′ : 6′-*trimethyl*cyclo*hexenyl*)-3-*methyldec-3-en-5-yn-2-ol* (4·7 g., 94%) as a pale yellow viscous oil, b. p. 85—90° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{16^\circ}$ 1·5124 (Found : C, 82·95; H, 11·1. $C_{20}H_{32}O$ requires C, 83·3; H, 11·2%). Light absorption : Maximum, 2290 A., ε = 16,500. Active hydrogen (Zerewitinoff) : The carbinol (176 mg.) gave 13·6 c.c. of methane at 25°/768 mm. (0·9 active hydrogen atom per mol.). The carbinol failed to yield a solid α-naphthylurethane. The carbinol (1·0 g.) in dry pyridine (10 c.c.) was treated with benzoyl chloride (0·6 g., redistilled), the mixture was kept for 24 hours at 20° in nitrogen, after which it was poured into water and extracted with ether. Evaporation of the washed and dried extract and distillation of the residue gave two fractions : (a) b. p. 90—100° (bath temp.)/10^{-4} mm. (0·2 g.), $n_{\mathrm{D}}^{18^\circ}$ 1·5255, consisting of a mixture with unchanged carbinol, and (b) b. p. 100—110° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{18^\circ}$ 1·5360, the *benzoate* (0·6 g.), a yellow viscous oil (Found : C, 82·8; H, 9·1. $C_{27}H_{35}O_2$ requires C, 82·6; H, 9·25%). Light absorption : Maximum, 2290 A., ε = 35,000.

1-(2′ : 6′ : 6′-*Trimethyl*cyclo*hexanyl*)-3-*methyldecan-2-ol*.—1-(2′ : 6′ : 6′-Trimethyl*cyclo*hexenyl)-3-methyldec-3-en-5-yn-2-ol (0·44 g.) in ethyl acetate (20 c.c.) was shaken with hydrogen in the presence of platinic oxide (0·1 g.) until absorption ceased. The carbinol required 135 c.c. of hydrogen (|= 3·75). Removal of catalyst and distillation of the residue afforded 1-(2′ : 6′ : 6′-*trimethyl*cyclo*hexanyl*)-3-*methyldecan-2-ol* (0·3 g., 67%) as a slightly viscous, colourless oil, b. p. 80° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4750 (Found : C, 80·8; H, 13·3. $C_{20}H_{40}O$ requires C, 81·0; H, 13·6%).

2-*Chloro*-1-(2′ : 6′ : 6′-*trimethyl*cyclo*hexenyl*)-3-*methyldec-3-en-5-yne*.—1-(2′ : 6′ : 6′-Trimethyl*cyclo*hexenyl)-3-methyldec-2-en-5-yn-4-ol (V) (2·5 g.) in ether (3 c.c.) was shaken with concentrated hydrochloric acid (10 c.c.) in nitrogen for 2 hours at 20°. The mixture was poured into water and the product isolated with ether. Removal of solvent from the washed and dried extract gave the *chloro-compound* (2·35 g., 85%) as a pale yellow oil, b. p. 65—70° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{21^\circ}$ 1·5210 (Found : C, 78·4; H, 10·15. $C_{20}H_{31}Cl$ requires C, 78·25; H, 10·2%). Light absorption : Maxima, 2390 A., ε = 17,000; 2420 A., ε = 17,000; 2810 A., ε = 4,500; 2900 A., ε = 4,000.

1-(2′ : 6′ : 6′-*Trimethyl*-$\Delta^{2'}$-cyclo*hexenyl*)-3-*methyldeca*-1 : 3-*dien-5-yne* (VII).—The above chloro-compound (1·2 g.) was heated with diethylaniline (20 c.c., redistilled) at 150—160° for 3 hours in nitrogen. A copious crystalline precipitate of diethylaniline hydrochloride separated on cooling. The bulk of the excess of diethylaniline was removed at 100°/4 mm., and the residue treated with ether and 2N-sodium hydroxide solution. The ethereal layer was washed with sodium hydroxide solution and the combined aqueous layers acidified with concentrated nitric acid and treated with an excess of 5% silver nitrate solution, giving a precipitate of silver chloride which after washing and drying at 100° weighed 0·55 g. (98% of theory). The ethereal extract was washed with 2N-hydrochloric acid, sodium bicarbonate solution, and water. Removal of solvent from the dried extract afforded 1-(2′ : 6′ : 6′-*trimethyl*-$\Delta^{2'}$-cyclo*hexenyl*)-3-*methyldeca*-1 : 3-*dien-5-yne* (0·9 g., 84%) as a pale yellow mobile oil, b. p. 70—75° (bath temp.)/10^{-4} mm., $n_{\mathrm{D}}^{21^\circ}$ 1·5466 (Found : C, 88·7; H, 11·2. $C_{20}H_{30}$ requires C, 88·8; H, 11·2%). On treatment with antimony trichloride in chloroform the hydrocarbon gave a purple colour changing to a deep blue.

Ozonolysis of 1-(2′ : 6′ : 6′-*Trimethyl*-$\Delta^{2'}$-cyclo*hexenyl*)-3-*methyldeca*-1 : 3-*dien*-5-*yne* (VII).—A solution of the hydrocarbon (1·7 g.) in dry carbon tetrachloride (40 c.c.) was treated with a slow stream of ozonised oxygen and the product isolated with ether as outlined by Heilbron, Johnson, and Jones (*J.*, 1939, 1560). Evaporation of the ethereal extracts gave an oil which was extracted with hot water (10 c.c.), and the filtered aqueous extract treated with an alcoholic solution of 2 : 4-dinitrophenylhydrazine sulphate. Crystallisation of the solid (150 mg.) so obtained, from methyl alcohol gave the 2 : 4-dinitrophenylhydrazone of *iso*geronic acid, m. p. 141°, undepressed on admixture with an authentic specimen (m. p. 140°). With the corresponding derivative of geronic acid a 20° depression in m. p. was observed.

9-*Methoxy*-1-(2′ : 6′ : 6′-*trimethyl*cyclo*hexenyl*)-3-*methyldeca*-2 : 7-*dien*-5-*yn*-4-*ol* (VIII).—A solution of 2-methoxyhex-3-en-5-yne (6 g., Heilbron, Jones, and Weedon, *J.*, 1945, 82) in dry ether (100 c.c.) was added to an ethereal solution of ethylmagnesium bromide (from 1·2 g. of magnesium) and the mixture was refluxed for 2·5 hours in nitrogen. A solution of the β-ionone C_{14} aldehyde (5·15 g., regenerated from the semicarbazone) in ether (100 c.c.) was added to the ice-cold Grignard solution during 1·5 hours and the mixture was then refluxed for 3 hours and stirred for a further 16 hours in nitrogen. Isolation by the usual method gave two fractions : (a) recovered aldehyde (1·2 g., 23%), b. p. 50° (bath temp.)/10^{-4} mm.; (b) 9-*methoxy*-1-(2′ : 6′ : 6′-*trimethyl*cyclo*hexenyl*)-3-*methyldeca*-2 : 7-*dien*-5-*yn*-4-*ol* (5·7 g., 94% yield calculated on reacted aldehyde), b. p. 94—98° (bath temp.)/10^{-4} mm., as a colourless liquid, $n_{D}^{17^\circ}$ 1·5300 (Found : C, 80·05; H, 10·2; $C_{21}H_{32}O_2$ requires C, 79·7; H, 10·2%). Active hydrogen (Zerewitinoff) : The carbinol (131 mg.) gave 10·1 c.c. of methane at 20°/759·5 mm. (1·0 active hydrogen atom per mol.). Light absorption : Maxima, 2235 and 2270 A., ε = 16,000 in each case. Inflexion, 2350 A., ε = 13,500.

9-*Methoxy*-1-(2′ : 6′ : 6′-*trimethyl*cyclo*hexenyl*)-3-*methyldeca*-3 : 7-*dien*-5-*yn*-2-*ol* (IX; R = OH).—The above methoxy-carbinol (VIII) (4 g.) was dissolved in sulphuric acid (500 c.c.; 1% w/v) containing acetone (250 c.c.) and the clear solution allowed to stand for 7 days at 20°. After pouring into water (5 l.), the product was isolated with ether. Evaporation of the washed and dried extract gave 9-*methoxy*-1-(2′ : 6′ : 6′-*trimethyl*cyclo*hexenyl*)-3-*methyldeca*-3 : 7-*dien*-5-*yn*-2-*ol* (3 g., 75%) as a colourless viscous liquid, b. p. 104—105° (bath temp.)/10^{-4} mm.; $n_{D}^{18^\circ}$ 1·5492 (Found : C, 79·85; H, 10·05. $C_{21}H_{32}O_2$ requires C, 79·7; H, 10·2%). Active hydrogen (Zerewitinoff) : The carbinol (132 mg.) gave 9·4 c.c. of methane at 16°/769 mm. (0·95 active hydrogen atom per mol.).

2-*Chloro*-9-*methoxy*-1-(2′ : 6′ : 6′-*trimethyl*cyclo*hexenyl*)-3-*methyldeca*-3 : 7-*dien*-5-*yne* (IX; R = Cl).—A solution of the unrearranged methoxy-carbinol (2·5 g.) in ether (7 c.c.) was shaken with concentrated hydrochloric acid (15 c.c.) for 3 hours at 20° in nitrogen. The yellow emulsion was poured into water and extracted thoroughly with ether. Removal of solvent from the washed and dried extract afforded the *chloro-compound* (2·4 g., 90%) as a pale yellow mobile oil, b. p. 65—66° (bath temp.)/10^{-4} mm., $n_{D}^{17^\circ}$ 1·5580 (Found : C, 75·55; H, 9·6. $C_{21}H_{31}OCl$ requires C, 75·3; H, 9·35%).

9-*Methoxy*-1-(2′ : 6′ : 6′-*trimethyl*-$\Delta^{2'}$-cyclo*hexenyl*)-3-*methyldeca*-1 : 3 : 7-*trien*-5-*yne* (X).—The chloro-compound (2 g.) was heated with diethylaniline (20 c.c., redistilled) for 3 hours at 160° in nitrogen. The cooled solution was diluted with ether and rapidly shaken several times with 2N-nitric acid to remove basic material. Addition of excess of 5% silver nitrate solution to the aqueous layers gave a precipitate of silver chloride which after washing and drying at 100° weighed 0·8 g. (93% of theory). The ethereal extract was washed and dried and on distillation gave the *methoxy-polyenyne* as a readily oxidised pale yellow oil (1·45 g., 81%), b. p. 95—96° (bath temp.)/10^{-4} mm., $n_{D}^{18^\circ}$ 1·5860 (Found : C, 80·3, 80·65, 81·0, 81·7; H, 9·65, 9·75, 9·95, 10·3. $C_{21}H_{30}O$ requires C, 84·5; H, 10·15%).

Ozonolysis of (X).—A solution of the methoxy-polyenyne (0·3 g.) in carbon tetrachloride (10 c.c.) was treated with ozonised oxygen for 7 hours; glacial acetic acid (10 c.c.) was then added and ozonolysis continued for a further 17 hours. Water (25 c.c.) and hydrogen peroxide (1 c.c. of 100-volume solution) were added to the product and the mixture was heated on the steam-bath for an hour under reflux. Water and acetic acid were distilled off under reduced pressure, and the product isolated with ether (Heilbron, Johnson, and Jones, *J.*, 1939, 1560). Evaporation of the ethereal extracts gave an oil which on treatment with 2 : 4-dinitrophenylhydrazine sulphate yielded an orange solid (120 mg., 35% of theory). Crystallisation from aqueous acetic acid gave orange micro-crystals of *iso*geronic acid 2 : 4-dinitrophenylhydrazone, m. p. 139—140°, undepressed on admixture with an authentic sample, but depressed by 26° when mixed with geronic acid 2 : 4-dinitrophenylhydrazone (m. p. 135°).

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