266. *Researches on Acetylenic Compounds. Part LXI.* The Synthesis of Three Polyacetylenic Esters.*

By Ian Bell, E. R. H. Jones, and M. C. Whiting.

Rational syntheses of three esters of the type (I), which include the first two natural polyacetylenic compounds to be isolated, are described. They

(I) $R{\cdot}C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH\overset{cis}{=}CH{\cdot}CO_2Me$ ($R = Me{\cdot}CH_2{\cdot}CH_2$, *cis*-$Me{\cdot}CH{=}CH$, and $Me{\cdot}C{\equiv}C$)

involve oxidative coupling of *cis*-pent-2-en-4-yn-1-ol with the appropriate acetylenic hydrocarbon, followed by cautious oxidation and methylation.

Among natural polyacetylenes two esters (I; $R = Me{\cdot}CH_2{\cdot}CH_2$ and *cis*-$Me{\cdot}CH{=}CH$) occupy a unique position, in that they were, by a wide margin, the first two to be isolated and given structural formulæ,[1,2] and are the most widely distributed compounds in this class. Their structures are known through degradative studies, and have been confirmed by the total synthesis of the corresponding Δ^2-*trans*-isomers, obtained from them by photoisomerisation.[3,4] A third member of the series, the ester (I; $R = Me{\cdot}C{\equiv}C$), is much less frequently encountered, but is present in *Artemesia vulgaris* L.[5] Its constitution has not been rigorously proved, but seemed highly probable on the basis of spectrographic evidence; the two *trans*-isomers, $Me{\cdot}[C{\equiv}C]_3{\cdot}CH{=}CH{\cdot}CO_2Me$ and $Me{\cdot}CH{=}CH{\cdot}[C{\equiv}C]_3{\cdot}CO_2Me$, have been synthesised [6a–c] and shown to be different.

Of these three esters, the least unsaturated was first isolated from *Lachnophyllum gossypinum* Bge,[1] and has since been found in a large number of *Erigeron* species; [7] ester (I; $R =$ *cis*-$Me{\cdot}CH{=}CH$) was isolated from scentless mayweed [2] [*Tripleurospermum maritimum* (L) Koch, formerly *Matricaria inodora L*], and from numerous *Erigeron* species.[7] They have become known as " lachnophyllum ester " and " matricaria ester," while the ester (I; $R = Me{\cdot}C{\equiv}C$) has been frequently referred to as " dehydromatricaria ester."

Only one compound (methyl *cis*-hex-2-en-4-ynoate) in which the characteristic grouping *cis*-$C{\equiv}C{\cdot}CH{=}CH{\cdot}CO_2Me$ occurs had previously been synthesised; [8] the method used is unlikely to be applicable to the natural esters. The preparation of *cis*-hex-3-en-5-yn-2-ol and *cis*-pent-2-en-4-yn-1-ol [9] suggested a more promising approach. The secondary alcohol is much the more accessible, and was investigated first, the *trans*-isomer being used in model experiments. Oxidation of the mixed isomers of the latter to hex-3-en-5-yn-2-one with chromic acid in acetone had already been reported.[10] Applied to the pure *trans*-isomer,[9] this technique gave a fair yield of a ketonic product, which, however, was difficult to separate from some unchanged alcohol. Applied to *cis*-hex-3-en-5-yn-2-ol [9] it gave a product consisting almost entirely of unchanged starting material, although the chromic acid underwent reduction; evidently a small proportion of the alcohol suffered extensive breakdown. Manganese dioxide oxidation [11] was then investigated, and gave a good yield of a product which crystallised readily. After recrystallisation, *trans*-hex-3-en-5-yn-2-one, m. p. 12·5—13°, had $\varepsilon_{max.}$ 16,500 at 2575 Å, as against $\varepsilon_{max.}$ 11,500 quoted by Bowden

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* Part LX, *J.*, 1958, 1054.

[1] Wiljams, Smirnov, and Golmov, *Zhur. obschchei Khim.*, 1935, **5**, 1195.

[2] N. A. Sørensen and Stene, *Annalen*, 1941, **549**, 80.

[3] Bruun, Haug, and N. A. Sørensen, *Acta Chem. Scand.*, 1950, **4**, 850.

[4] Bruun, Christensen, Haug, J. S. and N. A. Sørensen, *ibid.*, 1951, **5**, 1244.

[5] Stavholt and N. A. Sørensen, *ibid.*, 1950, **4**, 1567.

[6] (*a*) Christensen and N. A. Sørensen, *ibid.*, 1952, **6**, 602; (*b*) J. S. Sørensen, Bruun, Holme, and N. A. Sørensen, *ibid.*, 1954, **8**, 26; (*c*) Bohlmann and Mannhardt, *Chem. Ber.*, 1955, **88**, 428.

[7] Tronvold, Nestvold, Holme, J. S. and N. A. Sørensen, *Acta Chem. Scand.*, 1953, **7**, 1375.

[8] Allan, Jones, and Whiting, *J.*, 1955, 1862.

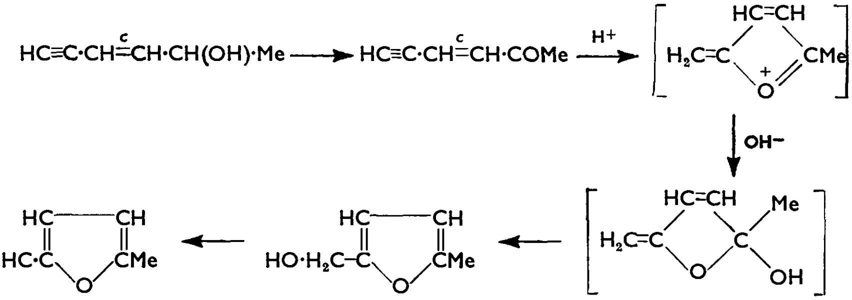
[9] Bell, Jones, and Whiting, *J.*, 1957, 2597.

[10] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

[11] Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094.

et al.;[10] evidently the specimen obtained earlier was a mixture of the ketone with up to 30% of the *cis*- and *trans*-alcohol. Oxidative cross-coupling with pent-1-yne gave *trans*-undec-3-ene-5 : 7-diyn-2-one, which underwent hypochlorite oxidation in methanol to give the *trans*-isomer of " lachnophyllum acid " (IV; R = $Me{\cdot}CH_2{\cdot}CH_2$) in 80% yield.

Manganese dioxide oxidation of *cis*-hex-3-en-5-yn-2-ol was now investigated, and was at once found to be much slower than that of the *trans*-form. It could be followed by the development of absorption at *ca.* 2600 Å, but the product always consisted of the desired ketone, starting-material, and a higher-boiling product. The last was isolated, and identified as 5-methylfurfuraldehyde, formed presumably by a reaction sequence of the annexed type:



The *cis*-ketone was readily identified by infrared bands at 1671 and at 769 and 753 cm.$^{-1}$, and the relatively weak absorption near 960 cm.$^{-1}$. Considerable difficulty, however, was encountered in purifying it, and results appeared to depend upon the state of the active manganese dioxide used; yields ranged from 20% downwards. A 2 : 4-dinitrophenylhydrazone was readily obtained, markedly different from that of the *trans*-ketone.[10]

Unfortunately, oxidative coupling of the *cis*-hex-3-en-5-yn-2-one with pent-1-yne gave, instead of the expected ketone, a product, m. p. 40°, which showed no C=O stretching band in the infrared spectrum, and had a single intense absorption maximum at 3320 Å. It had clearly been formed by some cyclisation related to that leading to 5-methylfurfuraldehyde. Hypochlorite oxidation of the C_6 ketone gave a moderate yield of pent-2-en-4-ynoic acid, but the *trans*-isomer predominated in the crude product, according to infrared results.

Because of the difficulties being encountered with *cis*-hexenynol, concurrent investigations on the use of *cis*-pent-2-en-4-yn-1-ol were begun. In the *trans*-series oxidation with manganese dioxide gave *trans*-pent-2-en-4-ynal, m. p. 18·5—19° (previously prepared in a crude state by Sondheimer [12] and by Bohlmann and Viehe [13]) and oxidative coupling with pent-1-yne led to *trans*-dec-2-ene-4 : 6-diynal. Oxidation to the *trans*-C_{10} acid with silver oxide proceeded smoothly. In the *cis*-series, however, oxidation of pent-2-en-4-yn-1-ol with chromic acid gave a mixture of *trans*-pent-2-en-4-ynoic acid and a liquid with vesicant properties; this was probably protoanemonin, formed by a cyclisation of the type discussed below. It seemed unlikely that *cis*-pent-2-en-4-ynal would be easily isolable, and the crossed-coupling reaction was therefore carried out first: *cis*-dec-2-ene-4 : 6-diyn-1-ol (II; R = $Me{\cdot}CH_2{\cdot}CH_2$) was readily obtained. Again, however, chromic acid oxidation gave only a very low yield of acidic material, without the expected ultraviolet absorption spectrum, and thus no doubt obtained by fission. Manganese dioxide oxidation, on the other hand, gave a 90% yield of the *cis*-aldehyde (III; R = $Me{\cdot}CH_2{\cdot}CH_2$). This showed no strong tendency either to isomerise to the *trans*-form or to cyclise, but on treatment with silver oxide it gave only the *trans*-acid, despite the exclusion of bright light. Molecular oxygen in the presence of manganese acetate [14] had no effect after 5 days. Finally the aldehyde was oxidised with chromic–sulphuric acid (1 equivalent) and the desired *cis*-acid

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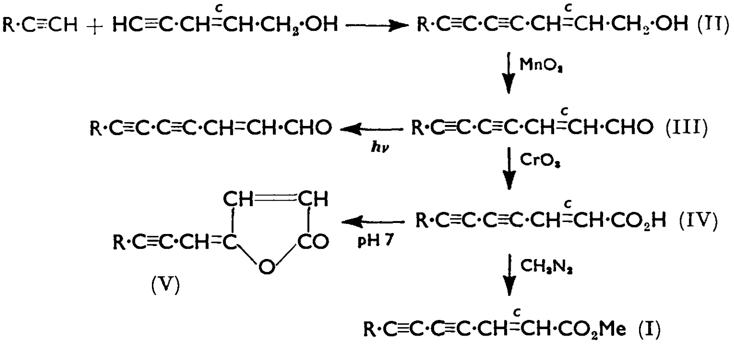
[12] Sondheimer, Ph.D. Thesis, London, 1948.
[13] Bohlmann and Viehe, *Chem. Ber.*, 1955, **88**, 1347.
[14] Owen, *J.*, **1943**, 463.

was obtained in about 25% yield. Methylation with diazomethane gave the corresponding ester, identical with the natural product kindly supplied by Professor Sørensen.

It is remarkable that *cis*-αβ-ethylenic γδ-acetylenic alcohols, whether primary or secondary, are so much less readily oxidised by chromic acid than the corresponding *trans*-forms. Possibly the use of manganese dioxide is successful because of an effectively small steric requirement in the removal of an α-proton by a centre of oxidative power adjacent to the site of adsorption. The use of manganese dioxide in a preliminary oxidation to the aldehyde stage may be generally useful in the process R·CH$_2$·OH ⟶ R·CO$_2$H, since direct treatment of the alcohol with chromic acid usually results in the formation of appreciable quantities of the ester, R·CH$_2$·O·CO·R.



Once the method had been worked out for the ester (I; R = Pr^n) it was applied to the other two esters; in these cases the two primary alcohols were obtained without difficulty, but the aldehydes (no doubt because they absorbed at longer wavelengths) were much more sensitive to photo-stereomutation. In each case it was preferable to use much more than one equivalent of chromic acid in the second stage. The triacetylenic acid was obtained, after the usual bicarbonate separation, as a mixture with a much larger quantity of a γ-lactonic impurity (V; R = Me·C≡C) characterised by an intense band at 1788 cm.$^{-1}$. (Similar contaminants were encountered in the other cases, but not in such large quantity.)

TABLE 1. C=O *stretching and* C–H *deformation frequencies* (*cm.*$^{-1}$) *in carbon disulphide.*

Compound		ν(C=O) (ε)		ν(C–H) (ε)	
HC≡C·CH=CH·CHO	*trans*	1689 (175)		955 (120)	
HC≡C·CH=CH·CO·Me	*trans*	1697 (140) ‡	1680 (170) ‡	957 (170)	[780 (40)]
	cis	1671 (190)		[958 (20)]	769 (40) *
C_3H_7·[C≡C]$_2$·CH=CH·CO·Me	*trans*	1691 (210)	1676 (240)	952 (200)	
[C≡C·CH=CH·CO·Me]$_2$	*trans*	1692 (280)	1675 (330) §		
C_3H_7·[C≡C]$_2$·CH=CH·CHO	*trans*	1688 (350)		948 (180)	
	cis	1678 (300)			757 (130)
CH_3·[C≡C]$_3$·CH=CH·CHO	*trans*	1682 (400)		949 (120)	
	cis	1677 (300)			753 (100)
C_3H_7·[C≡C]$_2$·CH=CH·CO$_2$H	*trans*	1684 (450)		953 (200)	
	cis	1690 (320)			816 (85)
CH_3·CH=CH·[C≡C]$_2$·CH=CH·CO$_2$H	(*cis*)	1695 (400)			816 (85) †
CH_3·[C≡C]$_3$·CH=CH·CO$_2$H	(*cis*)	1680 (s)			818 (m.)
C_3H_7·[C≡C]$_2$·CH=CH·CO$_2$Me	(*cis*)	1730 (270)	1715 (240)		809 (150)
CH_3·CH=CH·[C≡C]$_2$·CH=CH·CO$_2$Me	(*cis*)	1728 (210)	1716 (220)		808 (145) †
CH_3·[C≡C]$_3$·CH=CH·CO$_2$Me	(*cis*)	1725 (260)	1712 (280)		806 (145)

* A band at 753 cm.$^{-1}$ is also present.

† Plus a band at ~720 cm.$^{-1}$ attributable to *cis*-CH$_3$·CH$_2$·CH=CH·C≡C·.

‡ The relative intensities of these two bands were unchanged in carbon tetrachloride or in chloroform.

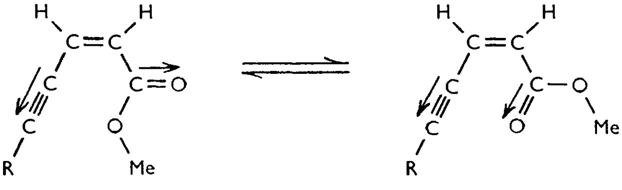
§ In CCl$_4$.

After various attempts to separate the acid from this lactone had failed, it was realised that the lactone was not formed in the chromic acid oxidation process, but rather in the separation of the acidic fraction; and when this step was omitted, the essentially pure triacetylenic *cis*-acid was obtained. It was then shown to undergo rapid cyclisation to the lactone, isolated as a crystalline solid, in neutral aqueous solution at room temperature. This reaction is discussed at greater length by Christensen, Sørensen, and the present authors,[15] who also report the identity of " Composit-cumulene " [16] with the corresponding lactone (V; R = *cis*-Me•CH=CH).

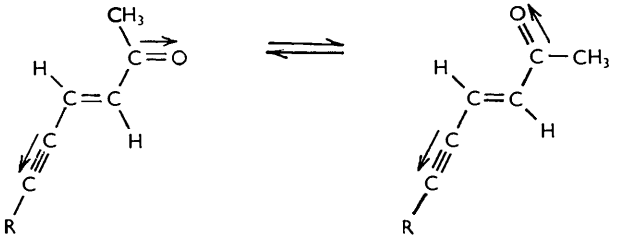
Methylation of the two *cis*-acids gave the methyl esters, identical with the naturally occurring compounds.

Infrared Absorption Spectra.—The spectra of most of the compounds discussed above were determined, and the more important results are summarised in Table 1. Conditions approximated to those of Part L,[17] but the intensities are generally lower than those reported in the previous paper by about 30%, presumably owing to cell path-length inaccuracy and/or lower resolution. Except where stated, carbon disulphide was used as solvent.

The splitting of the C=O stretching band in unsaturated carbonyl compounds was discovered by Allan, Meakins, and Whiting,[17] in the case of esters *cis*-$R{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CO_2Me$, and independently by Allen and Bernstein [18] in the case of furfuraldehyde. Both groups explained the effect as due to conformational isomerism, and this now appears to be well established.[19] The present results modify the situation in that they show that dipole interactions, such as must occur with the esters of type (I), are not responsible for the different frequencies of the *cisoid* and *transoid* forms.



transoid *cisoid*



Whereas in the esters the C–C≡C and C=O dipoles are at 120° and 0° in the *transoid* and *cisoid* forms, respectively, in the two forms of *trans*-hex-3-en-5-yn-2-one they are both at 120°. Yet this ketone also shows two bands, of comparable intensity, and separated by about the same frequency difference; evidently the two different frequencies of the conformational isomers are a direct consequence of the relative orientation of the C=C and C=O bonds. As was observed for the *cis*-esters, changes in the rest of the molecule do not appreciably affect the carbonyl bands. In substances $R{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}COX$, this phenomenon is observed in the *cis*-esters, but not the *trans*-; in the *trans*-ketones, but not the *cis*-; and in neither of the aldehydes. The last fact is readily intelligible, since the second condition for its observation is that the two conformational isomers should be present in comparable

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[15] Christensen, N. A. Sørensen, Bell, Jones, and Whiting, " Festschrift Arthur Stoll," Basel, 1957, p. 545; see also Christensen, *Acta Chem. Scand.*, 1957, **11**, 572.

[16] Sørensen and Stavholt, *Acta Chem. Scand.*, 1950, **4**, 1080.

[17] Allan, Meakins, and Whiting, *J.*, 1955, 1874.

[18] Allen and Bernstein, *Canad. J. Chem.*, 1955, **33**, 1055.

[19] R. N. Jones, Forbes, and Mueller, *ibid.*, 1957, **35**, 504; Cromwell, Abs. Paper, 131st Meeting, Amer. Chem. Soc., April 1957 (p. 82-o).

quantity, and in the aldehydes (*cis* or *trans*), as distinct from the esters and ketones, there is a considerable steric advantage for the *transoid* forms, which are thus probably present in large excess.

TABLE 2. *Ultraviolet absorption spectra of* C_5 *and* C_6 *intermediates.*

		Å	
trans-Pent-2-en-4-ynal	(alcohol)	Max., 2575 (ε 18,000) [a]	
	(hexane)	Max., 2455 (ε 21,000) Max., 2575 (ε 20,500)	Min., 2530 (ε 17,500)
trans-Hex-3-en-5-yn-2-one	(alcohol)	Max., 2575 (ε 16,500) [b] Max., 3300 (ε 56)	Min., 3030 (ε 38)
cis-Hex-3-en-5-yn-2-one	(alcohol)	Max., 2560 (ε 10,500)	

[a] For a crude specimen (no refractive index, m. p., or analytical data), Bohlmann and Viehe (*Chem. Ber.*, 1955, **88**, 1347) give $\lambda_{max.}$ 2570 A, ε 10,800 in methanol. [b] For a specimen obtained from the mixed isomers of hex-3-en-5-yn-2-ol and chromic acid, Bowden, Heilbron, Jones, and Weedon (*J.*, 1946, 39) give $\lambda_{max.}$ 2550 Å, ε 11,500.

In the acetylenic αβ-ethylenic aldehydes and ketones a *cis*-ethylenic linkage displaces the carbonyl band further to lower frequency than a *trans*-bond, in contrast to the results for esters.[17] The C–H out-of-plane deformation frequencies amplify the earlier results.[17]

Ultraviolet Absorption Spectra.—Data for the simple intermediates are compared, in Table 2, with each other and with earlier values.

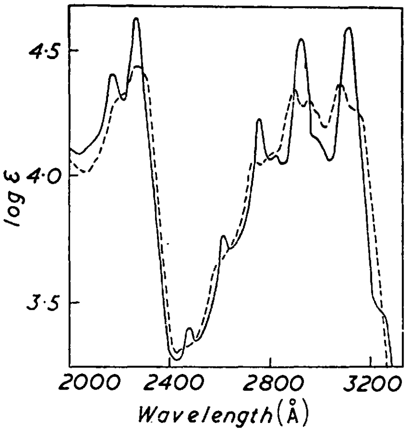

FIG. 1. ——— *Dec-2-ene-4 : 6-diynal (in hexane).*
– -- – – *Undec-3-ene-5 : 7-diyn-2-one (in hexane).*

The spectra of *trans*-dec-2-en-4 : 6-diynal (IV) and of the corresponding methyl ketone are of especial interest and are illustrated (Fig. 1). Broadly, they are typical of diacetylenes with one or two ethylenic or carbonyl-containing end-groups; that is, two series of bands are present, one beginning at ~3100 Å (*A*,*B* ···bands), one at about 2300 Å (*L*,*M* ···bands), each group spaced at about 2000 cm.$^{-1}$. In the ketone, however, the bands of the *A* group are each doubled, as though two components were present, one absorbing at about 50 Å longer than the other, and present in rather smaller concentration or having a rather smaller extinction coefficient. The aldehyde, on the other hand, shows at first sight a normal spectrum; yet minor maxima and inflexions are present which suggest that a second component, absorbing at longer wavelengths, is present in much smaller quantity than the main component. The *L*-band groups reveal a similar, if less pronounced, effect. Clearly these effects can be correlated with the infrared evidence for the presence of two conformational isomers in comparable quantities for the ketone, but in very unequal quantities for the aldehyde. This may be true quite generally for ethylenic carbonyl compounds, but the majority have ultraviolet absorption spectra so devoid of vibrational fine structure, even in non-polar solvents, that the superposition of two similar spectra separated by a small interval is not detectable. If the C=O stretching frequencies also differed very little, the phenomenon would be difficult to observe.

Table 3 lists the spectra of the various C_{10} intermediates and by-products which have not already been reported by the Trondheim school, with whose results our other data are in good agreement. Fig. 2 illustrates the absorption spectra of the 2 : 4-dinitrophenylhydrazones of the *cis*- and *trans*-aldehydes (III), which show, in a remarkably clear case, the appearance of bands attributable to a partial chromophore ($-C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH{=}CH-$) when the linear *trans*-$C{\equiv}C{\cdot}C{\equiv}C{\cdot}CH{=}CH{\cdot}CH{=}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$ system is replaced by the bent (and perhaps partly non-coplanar) *cis*-analogue.

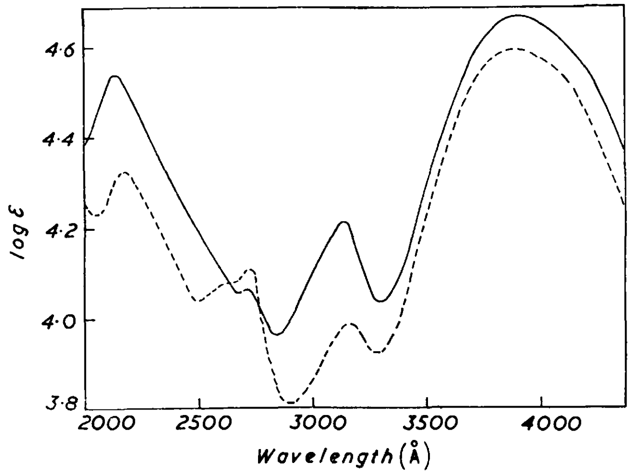

FIG. 2. 2 : 4-*Dinitrophenylhydrazone of* trans(———) *and* cis(– – – –)-*dec-2-ene-4* : 6-*diynal, in alcohol.*

N.B. Hex-1-en-3 : 5-diyne has absorption maxima at 2770, 2620, 2480, and 2360 Å, respectively, with ε values of the order of 10^3—10^4 (Cook, Jones, and Whiting, unpublished work).

TABLE 3. *Ultraviolet spectra of* C_{10} *intermediates and symmetrical by-products.*

Max. (Å)	$10^{-3}\varepsilon$	Min. (Å)	$10^{-3}\varepsilon$
$(cis\text{-}HO{\cdot}CH_2{\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot})_2$			
2310	28	2330	27·5
2375	29	2435	21
2470	24	—	—
2625	7·4	2700	4·4
2775	14·5	2860	5·5
2945	22·5	3050	4·5
3135	18·5		
$(trans\text{-}Me{\cdot}CO{\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot})_2$			
2235	25	2345	16
2780	27·5	2960	16·5
3060	20·5	3140	18·5
3260	26·5	3385	18·0
3490	23·5		
cis : $cis\text{-}CH_3{\cdot}CH{=}CH{\cdot}[C{\equiv}C]_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH$			
2180	26·5	2215	26
2370	30	2435	22
2465	24	2560	3·5
2625	7·4	2705	4·5
2775	14	2870	5·5
2945	21·5	3055	4·4
3140	18		
$cis\text{-}C_3H_7{\cdot}[C{\equiv}C]_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH$			
2300	2·5	2225	1·8
2415	5·2	2340	1·6
2540	11·5	2460	2·8
2685	19	2610	4·0
2845	15·5	2770	3·2
$cis\text{-}C_3H_7{\cdot}[C{\equiv}C]_2{\cdot}CH{=}CH{\cdot}CHO$			
2205	15	2075	8
2295	20	2245	12
2485	1·9	2450	1·7
2780	10	2505	1·8
2835	8·9	2820	8·5
2950	21	2870	8·0
3140	23	3060	8·0

EXPERIMENTAL

General techniques for manipulating low-melting, unstable substances were described in Part XLIX of this Series.[8] It was, however, necessary also to exclude light as completely as possible from all operations when polyacetylenic *cis*-αβ-ethylenic aldehydes, esters, and acids were handled, since these showed a tendency to isomerise to the *trans*-isomers.

Manganese dioxide was prepared by the method of Attenburrow *et al.*[11] and was washed by decantation for several days. Thorough washing was essential for high activity; after final washings with methanol and ether the oxide was dried overnight at 100°.

Silver oxide was precipitated from aqueous solution, washed with water, methanol, and ether, and dried at 20°/10 mm.

Light petroleum refers to the fraction of b. p. 60—80°. Ultraviolet and infrared spectra were determined with a Unicam S.P. 500 and a Perkin-Elmer 21 Spectrophotometer, respectively, the solvents being alcohol, and carbon disulphide, unless otherwise stated.

trans-*Hex-3-en-5-yn-2-one*.—*trans*-Hex-3-en-5-yn-2-ol [9] (4·8 g.), active manganese dioxide (48 g.), and methylene dichloride (400 c.c.) were shaken together for 2 hr. at 18°, the reaction being followed by the increasing absorption-intensity at *ca.* 2600 Å, and diminishing intensity at *ca.* 2200 Å. When no further change was observed (variable, but usually 2—24 hr.) the manganese dioxide was filtered off and washed with hot methylene dichloride. Removal of the solvent through a Dufton column and distillation of the residue gave the essentially pure *ketone* (3·3 g., 70%), b. p. 60°/20 mm., which solidified at 0°. Three crystallisations from pentane gave needles, m. p. 12·5—13°, n_D^{20} 1·4990 (Found: C, 76·85; H, 6·8. C_6H_6O requires C, 76·55; H, 6·45%). (For their specimen of hex-3-en-5-yn-2-one Bowden *et al.*[10] give b. p. 60—63°/20 mm., n_D^{16} 1·4954.) The 2 : 4-dinitrophenylhydrazone had m. p. 182° (decomp.) [lit., m. p. 181° (decomp.)].

Oxidation of cis-*Hex-3-en-5-yn-2-ol*.—The alcohol [9] (9·6 g.), manganese dioxide (96 g.), and methylene dichloride (800 c.c.) were shaken at 20° for 100 hr. After filtration and thorough washing of the residue, the solvent was removed and the residual liquid was distilled, giving the crude *cis*-ketone (1·9 g.), b. p. 48—54°/14 mm., n_D^{20} 1·4966—1·5000, and 5-methylfurfuraldehyde (1·1 g.), b. p. 66°/14 mm., n_D^{20} 1·5264. Careful redistillation gave cis-*hex-3-en-5-yn-2-one*, n_D^{20} 1·4930 (3 fractions) (Found: C, 76·5; H, 6·85%), and the aldehyde, n_D^{25} 1·5270 (Found: C, 65·4; H, 5·7. Calc. for $C_6H_6O_2$: C, 65·45; H, 5·5%). Light absorption: max. 2250 and 2835 Å; min., 2100 and 2415 Å (10^{-3} ε 2·8, 17, 1·8, 0·9, respectively). For the aldehyde Rinkes [20] gives b. p. 83—85°/15 mm.

The 2 : 4-*dinitrophenylhydrazone* of the *cis*-ketone formed orange-red plates, m. p. 152—153°, from ethanol (Found: C, 52·45; H, 3·7. $C_{12}H_{10}O_4N_4$ requires C, 52·55; H, 3·7%). The 2 : 4-*dinitrophenylhydrazone* of 5-methylfurfuraldehyde separated from ethanol in red needles, m. p. 211·5—213·5° (Found: C, 49·9; H, 4·1. $C_{12}H_{10}O_5N_4$ requires C, 49·65; H, 3·5%), and had light absorption max. 2200, 2640, 3000, and 3830 Å, min. 2110, 2410, 2880, and 3210 Å (10^{-3} ε 16, 19·5, 8·8, 16, 28·5, 15, 13·5, 8, and 5·3, respectively).

5-*Methylfuroic Acid*.—5-Methylfurfuraldehyde (100 mg.), obtained as above, freshly precipitated silver oxide (500 mg.), and methanol (10 c.c.) were shaken together for 18 hr. at 20°. Isolation of the acidic fraction with ether gave the acid (91 mg.), m. p. 108·5—109·5° after crystallisation from light petroleum (Hill and Sawyer [21] gave m. p. 108—109°).

trans-*Pent-2-en-4-ynal*.—*trans*-Pent-2-en-4-yn-1-ol (4·1 g.), manganese dioxide (41 g.), and methylene dichloride (350 c.c.) were shaken at 20° for 8 hr.; light-absorption data then indicated complete reaction. The manganese dioxide was filtered off and washed well. Removal of solvent and distillation of the residue gave the aldehyde (1·7 g., 43%), b. p. 61—62°/54 mm., $n_D^{21.5}$ 1·5128—1·5132, m. p. 17°. Crystallisation from pentane gave long needles, m. p. 18·5—19°, which gave the expected ultraviolet and infrared spectra but were too unstable to yield satisfactory analytical data (Sondheimer [12] gives b. p. 82—84°/135 mm., n_D^{30} 1·5030). The 2 : 4-*dinitrophenylhydrazone* formed brown-red needles from ethanol which decomposed above 150° without melting, as stated by Bohlmann and Viehe [13] (Found: C, 51·2; H, 3·5. $C_{11}H_8O_4N_4$ requires C, 50·8; H, 3·1%).

trans-*Dec-2-ene-4* : 6-*diynal*.—The above aldehyde (1·4 g.) and pent-1-yne (5·1 g.) were mixed and added to a stirred suspension of cuprous chloride (23·5 g.) and ammonium chloride (37 g.) in water (120 c.c.), which had been brought to pH 3 by addition of a little concentrated hydrochloric acid. After 15 min. the mixture was cooled to 0°, while hydrogen peroxide (" 100-vol."; 50 c.c.) was added slowly below the liquid surface, at such a rate that the temperature did not rise above 10° (2 hr.), the mixture becoming bright green. After a further hour at 5°, phosphoric acid (10%; 200 c.c.) was added and the neutral product was isolated with ether (no appreciable acidic fraction was obtained). Light petroleum was added to the residue, and the insoluble *trans* : *trans*-deca-2 : 8-diene-4 : 6-diynedial (390 mg.), m. p. 135—140°, was removed [Weedon [22] gives m. p. 144° (decomp.)]. The residue was distilled, to give

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[20] Rinkes, *Org. Synth.*, 1934, **14**, 62.

[21] Hill and Sawyer, *Amer. Chem. J.*, 1898, **20**, 171.

[22] Weedon, *J.*, 1954, 4168.

deca-4 : 6-diyne, which was discarded, and essentially pure trans-*dec*-2-*ene*-4 : 6-*diynal* (1·16 g.), b. p. 92—100° (bath-temp.)/0·1 mm., which after redistillation had n_D^{17} 1·6004, m. p. 2—3° (Found: C, 81·75; H, 7·3. $C_{10}H_{10}O$ requires C, 82·15; H, 6·9%). The 2 : 4-*dinitrophenylhydrazone* formed brick-red needles, m. p. 195—196°, from ethanol (Found: C, 58·85; H, 4·45. $C_{16}H_{14}O_4N_4$ requires C, 58·9; H, 4·3%).

trans-*Undec*-3-*ene*-5 : 7-*diyn*-2-*one*.—Oxidative coupling, as above, of *trans*-hex-3-en-5-yn-2-one (3·1 g.) and pent-1-yne (9·2 g.) using cuprous chloride (41·5 g.), ammonium chloride (67 g.), and hydrogen peroxide (" 100-vol.; " 60 c.c.), gave a neutral fraction from which was precipitated trans : trans-*dodeca*-3 : 9-*diene*-5 : 7-*diyne*-2 : 11-*dione* (570 mg.), m. p. 138—138·5° after recrystallisation from benzene–light petroleum (Found: C, 77·2; H, 5·6. $C_{12}H_{10}O_2$ requires C, 77·4; H, 5·4%).

The light petroleum filtrates were evaporated and the residue was distilled, giving decadiyne and the essentially pure ketone (2·6 g.), b. p. 100° (bath-temp.)/0·05 mm. After crystallisation from pentane trans-*undec*-3-*ene*-5 : 7-*diyn*-2-*one* formed thick needles, m. p. 17—17·5°, n_D^{22} 1·5812 (Found: C, 82·6; H, 7·75. $C_{11}H_{12}O$ requires C, 82·45; H, 7·5%). The 2 : 4-*dinitrophenylhydrazone* formed bright red prisms, m. p. 135—135·5°, from ethanol (Found: C, 60·25; H, 4·75. $C_{17}H_{16}O_4N_4$ requires C, 60·0; H, 4·75%).

trans-*Dec*-2-*ene*-4 : 6-*diynoic Acid*.—(*a*) The corresponding aldehyde (500 mg.), silver oxide (1·4 g.), and potassium hydroxide (200 mg.) in methanol (10 c.c.) were shaken at 20° for 24 hr. The acid fraction (290 mg.) was isolated and crystallised from aqueous ethanol (charcoal), giving plates, m. p. 124—125° (Holme and Sørensen [23] give m. p. 123·5—124·5° for the acid prepared from the naturally occurring *trans*-ester).

(*b*) The corresponding methyl ketone (320 mg.) in methanol (90 c.c.) and water (7·5 c.c.) was treated with 4·4N-sodium hypochlorite (2·5 c.c.). The reaction was followed spectroscopically, and was almost complete in 3 hr. at 20°. Isolation of the acidic fraction (260 mg.; m. p. 116—122°) and crystallisation from light petroleum gave needles, m. p. and mixed m. p. 124—125°.

cis-*Dec*-2-*ene*-4 : 6-*diyn*-1-*ol*.—A mixture of *cis*-pent-2-en-4-yn-1-ol (1·0 g.) pent-1-yne (6·4 g.), cuprous chloride (27 g.), ammonium chloride (43 g.), and water (150 c.c.) was treated with hydrogen peroxide (" 100-vol.; " 40 c.c.). Isolation of the product with ether and removal of the solvent left a residue which was extracted with warm pentane (10 × 100 c.c.); the insoluble residue (146 mg.; m. p. 45—46°) crystallised from ether–pentane, giving cis : cis-*deca*-2 : 8-*diene*-4 : 6-*diyne*-1 : 8-*diol*, m. p. 62—63° (Found: C, 74·15; H, 6·3. $C_{10}H_{10}O_2$ requires C, 74·05; H, 6·2%).

Evaporation of the pentane extracts and distillation of the residue gave much deca-4 : 6-diyne, b. p. 65—75° (bath-temp.)/0·4 mm., which was discarded, and cis-*dec*-2-*ene*-4 : 6-*diyn*-1-*ol* (970 mg.), b. p. 121—126° (bath-temp.)/0·4 mm., n_D^{17} 1·5630 (Found: C, 81·4; H, 8·3. $C_{10}H_{12}O$ requires C, 81·05; H, 8·15%). The 3 : 5-*dinitrobenzoate*, prepared by the method of Mills,[24] formed needles, m. p. 91—92° (Found: C, 59·75; H, 4·3. $C_{17}H_{14}O_6N_2$ requires C, 59·65; H, 4·1%).

cis-*Dec*-2-*ene*-4 : 6-*diynoic Acid*.—*cis*-Dec-2-ene-4 : 6-diyn-1-ol (105 mg.) and active manganese dioxide (1·0 g.) in methylene chloride (15 c.c.) were stirred rapidly at room temperature. The reaction was followed spectroscopically and was complete in 2 hr. The manganese dioxide was filtered off and thoroughly washed with boiling solvent. Evaporation left the *cis*-aldehyde (93 mg.) which in another experiment was purified by chromatography and obtained as a light yellow oil, n_D^{19} 1·5780, characterised by its ultraviolet and infrared spectra and as its 2 : 4-*dinitrophenylhydrazone*, which formed fine red needles, m. p. 112—113° (Found: C, 58·75; H, 4·45. $C_{16}H_{14}O_4N_4$ requires C, 58·9; H, 4·3%).

The aldehyde was dissolved in pure acetone (15 c.c.), and the solution was stirred rapidly at −5° while a solution of chromic acid (6N in 12N-sulphuric acid; 0·22 c.c.) was added, one micro-drop at a time, from a capilliary pipette during 30 min. Stirring at −5° was maintained for 1 hr., the mixture becoming green. Water (40 c.c.) was added, and the mixture was extracted with ether; the extracts were washed with saturated aqueous potassium hydrogen carbonate solution. After drying ($MgSO_4$), the ether solution was evaporated to give recovered aldehyde (51 mg.), shown by its ultraviolet and infrared spectra to be essentially pure. The bicarbonate extracts were cautiously acidified with 2N-sulphuric acid in the presence of ether; the dried extract was evaporated, giving a semi-solid residue (38 mg.) which could not be purified

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[23] Holme and Sørensen, *Acta Chem. Scand.*, 1954, **8**, 280.

[24] Mills, *J.*, 1951, 2332.

by crystallisation. This was dissolved in ether (40 c.c.) and extracted with a solution of potassium hydrogen carbonate (6 mg.) in water (10 c.c.); evaporation of the ether now gave a solid residue (30 mg.; m. p. 59—65°) which crystallised from pentane at low temperatures, then at 20° from light petroleum (b. p. 60—80°), to give the acid as prisms, m. p. 72—74°. Further crystallisation, however, gave fine needles, m. p. 59—60°, evidently a polymorphic form (Found: C, 73·55; H, 6·4. Calc. for $C_{10}H_{10}O_2$: C, 74·05; H, 6·2%). Holme and Sørensen [23] give m. p. 72—73° (indistinct) for the acid prepared from the natural ester.

Methyl cis-*Dec-2-ene-4 : 6-diynoate* (" *Lachnophyllum Ester* ").—The above acid (30 mg.) in dry ether (10 c.c.) was treated with the theoretical quantity of dry ethereal diazomethane and kept at 17° for 20 min. in the dark. The solution was evaporated to dryness, ether (40 c.c.) was added and, after being washed with saturated potassium hydrogen carbonate and dried, the solution was again evaporated. The residue (30 mg.; m. p. 24—30°) was crystallised four times from pentane at −60°, to give the ester (10 mg.) as fine needles, m. p. 31—32°, undepressed on admixture with the natural product (Found: C, 74·65; H, 6·85. Calc. for $C_{11}H_{14}O_2$: C, 74·95; H, 6·85%).

cis : cis-*Deca-2 : 8-diene-4 : 6-diyn-1-ol.*—Oxidative coupling of *cis*-pent-2-en-4-yn-1-ol (500 mg.) and *cis*-pent-2-en-4-yne (4 g.), using cuprous chloride (17·5 g.), ammonium chloride (27·5 g.), water (100 c.c.), and hydrogen peroxide (" 100-vol.; " 20 c.c.) gave, after isolation of the pentane-soluble fraction, a residue which was distilled at 10^{-3} mm. *cis* : *cis*-Deca-2 : 8-diene-4 : 6-diyne had b. p. 47—60° (bath-temp.), n_D^{19} 1·6054, and cis : cis-*deca-2* : *8-diene-4* : *6-diyn-1-ol* (420 mg.), b. p. 112—114° (bath-temp.), n_D^{19} 1·6170—1·6174 (Found: C, 82·05; H, 7·5. $C_{10}H_{10}O$ requires C, 82·15; H, 6·9%).

Methyl cis : cis-*Deca-2 : 8-diene-4 : 6-diynoate* (" *Matricaria Ester* ").—The above alcohol (42 mg.) was oxidised with manganese dioxide (400 mg.) in methylene dichloride (20 c.c.) for 2 hr. at 17°, giving the crude aldehyde (40 mg.). This was dissolved in acetone (15 c.c.); chromic acid (0·35 c.c.; 6N in 12N-sulphuric acid) was added at 17° during 1 hr. Isolation of the acidic fraction *via* ice-cold saturated potassium hydrogen carbonate solution, then acidification with cooled dilute sulphuric acid in the presence of ether, gave a residue (12 mg.), which was repeatedly crystallised from ether–pentane, to give *cis* : *cis*-deca-2 : 8-diene-4 : 6-diynoic acid (5 mg.), m. p. 96·5—99·5°. Methylation with diazomethane, as above, and chromatography on neutral alumina gave, in the benzene eluate, a residue (4 mg.; m. p. 30—33°); four recrystallisations from pentane at −45° gave the ester (2·8 mg.) as long needles, m. p. 34—35°, undepressed on admixture with the natural ester (Found: C, 75·4; H, 6·0. Calc. for $C_{11}H_{10}O_2$: C, 75·85; H, 5·8%) (Sørensen and Stene [2] give m. p. 37°, but we were unable to raise the m. p. of the natural material above 34—35°; for the derived acid they give m. p. 98—99°).

cis-*Dec-2-ene-4 : 6 : 8-triyn-1-ol.*—*cis*-Pent-2-en-4-yn-1-ol (1·0 g.) and crude penta-1 : 3-diyne [8] (8·0 g.; n_D^{17} 1·481) were coupled oxidatively by means of cuprous chloride (35 g.), ammonium chloride (55 g.), water (100 c.c.) and hydrogen peroxide (" 100-vol.; " 50 c.c.). Isolation of the product and chromatography on active alumina gave much deca-2 : 4 : 6 : 8-tetrayne and (eluted with 10% methanol in ether) the crude alcohol (540 mg.; m. p. 35—40°). After five crystallisations from ether–pentane at −30° the *alcohol* formed plates, m. p. 41—42·5° (Found: C, 83·55; H, 5·75. $C_{10}H_8O$ requires C, 83·3; H, 5·6%). It rapidly became blue in light.

Methyl cis-*Dec-2-ene-4 : 6 : 8-triynoate.*—The above alcohol (120 mg.) was oxidised with manganese dioxide (1·2 g.) in methylene dichloride (30 c.c.) at 20° for 2 hr. Isolation of the aldehyde gave a solid, m. p. 48—58° (which on another occasion was recrystallised in diffused daylight and suffered isomerisation to the *trans*-form, m. p. 93—106°, as shown by the substitution of a band at 949 cm.$^{-1}$ for that at 743 cm.$^{-1}$). It was dissolved in acetone (25 c.c.) and treated with chromic acid (0·78 c.c.; 6N in 12N-sulphuric acid), added during 1 hr. at 16°. Water was added and the product was isolated with ether, which was removed to leave a brown residue. Crystallisation from ether–pentane gave, after removal of brown polymeric material (17 mg.), the crude acid (74 mg.), m. p. 145° (decomp.).

This acid (45 mg.) was treated with diazomethane, as above. Chromatography and crystallisation from pentane at −35° gave the *ester* (30 mg.; m. p. 111—113°), which after treatment with norite and further crystallisation formed thick pale yellow needles, m. p. 114—115° (Found: C, 77·15; H, 4·7. Calc. for $C_{11}H_8O_2$: C, 76·75; H, 4·7%). A sample of the natural ester had m. p. 114—115°, undepressed on admixture with the synthetic product (Stavholt and Sørensen [5] give m. p. 113°).

Lactone of 4-*Hydroxydeca*-2 : 4-*diene*-6 : 8-*diynoic Acid.*—The *lactone* was first obtained from the products of several experiments in which *cis*-dec-2-en-4 : 6 : 8-triynal was oxidised with chromic acid and an attempt was made to isolate the acidic fraction *via* potassium hydrogen carbonate solution. It formed plates, m. p. 135—136° (Found: C, 75·9; H, 4·25. $C_{10}H_6O_2$ requires C, 75·95; H, 3·8%).

cis-Dec-2-en-4 : 6 : 8-triynoic acid (5·0 mg.) was added to saturated potassium hydrogen carbonate solution (10 c.c.). After 5 min. at 20° the solution was extracted with ether; the resultant solid (2·8 mg.) had essentially the same infrared spectrum, characterised by sharp and intense bands at 1788, 1330, 1095, 1059, 934, 867, 820, and 757 cm.$^{-1}$, as for the pure lactone.

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