

Researches on Acetylenic Compounds. Part XLIX. The Preparation and Ultraviolet Absorption Spectra of the Stereoisomeric Conjugated Hexadienoic and Hexenynoic Acids.*

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All the possible stereoisomeric forms of the conjugated hexadienoic and hexenynoic acids have been prepared. Their properties, and in particular their ultraviolet absorption spectra, have been compared with those of hexa-2 : 4-dienoic, but-2-ynoic, and the two but-2-enoic acids.

THE specificity of palladium catalysts, in particular the lead-poisoned form (Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446), for the partial hydrogenation of acetylenic linkages has permitted syntheses of several conjugated polyenes with *cis*-linkages in predetermined positions. These products, however, have all been complex compounds related to the carotenoids, with the exception of the *cis-cis*- and *cis-trans*-diphenylbuta-1 : 3-dienes prepared by Pinkard, Wille, and Zechmeister (*J. Amer. Chem. Soc.*, 1948, **70**, 1938), in which steric hindrance to the coplanarity of the chromophore is also involved. We now describe syntheses of the stereoisomers of *trans-trans*-hexa-2 : 4-dienoic (sorbic) acid, and of the four related hexenynoic acids. These substances were chosen because they fairly represent

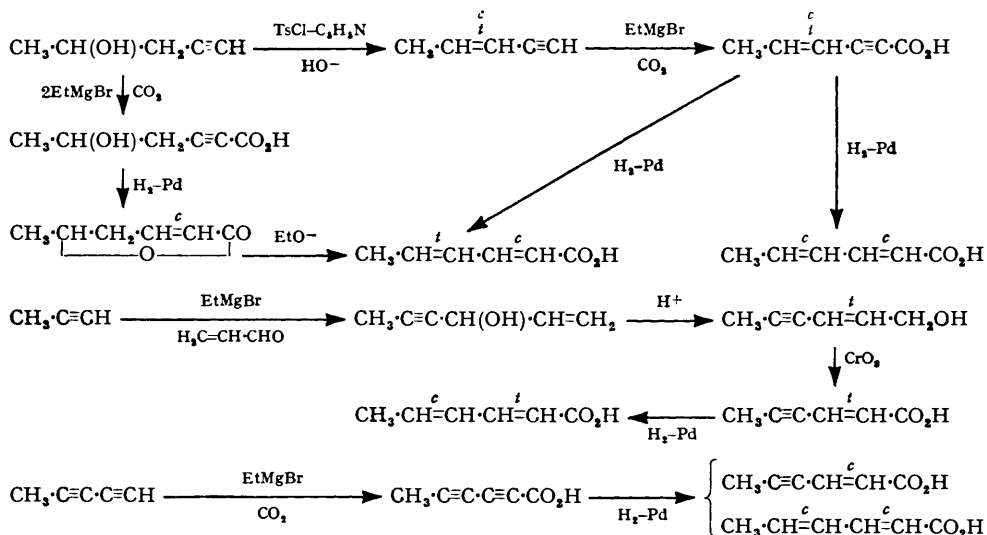
* Part XLVIII, *J.*, 1954, 3212.

simple conjugated aliphatic *cis*-ethylenes, and would probably crystallise and so be obtainable pure even though unstable. The spectroscopic data reported here and in the following paper would also be useful in diagnostic problems involving naturally-occurring conjugated polyene and polyenyne esters. Parallel and independent work by Crombie (*J.*, 1955, 1007) on the synthesis of the decadienoic acids has recently been published.

Of the nine C₆-acids with ethylenic and/or acetylenic bonds in the αβ- and the γδ-position, the *trans-trans*-diene has been known for many years, and hexa-2 : 4-dienoic acid has been briefly described by Schlubach and Wolf (*Annalen*, 1950, 568, 141) and by Jones, Whiting, Armitage, Cook, and Entwistle (*Nature*, 1951, 168, 900), who treated the bromomagnesium derivative of penta-1 : 3-diyne with carbon dioxide. When *cis*- and *trans*-pent-3-en-1-yne (Allan and Whiting, *J.*, 1953, 3314) were treated similarly the *cis*- and *trans*-hex-4-en-2-yenoic acids were obtained. Semihydrogenation (Lindlar, *loc. cit.*) of the *cis*-acid readily gave hexa-*cis*-2 : *cis*-4-dienoic acid, m. p. 81.5—82.5°, while the *trans*-isomer gave the expected hexa-*cis*-2 : *trans*-4-dienoic acid, m. p. 31—34°, which was much less easily isolated. In the latter case a little *trans-trans*-hexadienoic acid was also obtained, in agreement with the view (see Raphael, "Acetylenic Compounds," Butterworth, 1955, p. 24) that a small proportion (~5%) of the *trans*-compound is normally formed in the semihydrogenation of acetylenic compounds. In both cases hexenoic and unchanged hexenylic acids were present in the crude product, but could be removed by distillation and recrystallisation until melting point and infrared absorption spectrum were constant.

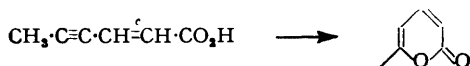
For the synthesis of *trans*-hex-2-en-4-yenoic acid, propyne—for which an improved preparative method is described—was condensed with acraldehyde, and the resulting alcohol was rearranged to hex-2-en-4-yn-1-ol, the *trans*-isomer being the main product (cf. Braude and Coles, *J.*, 1951, 2085). Oxidation with chromic and sulphuric acids in aqueous acetone (Heilbron, Jones, and Sondheimer, *J.*, 1947, 1586) gave the corresponding acid, whose *trans*-configuration, deduced from the method of synthesis, was confirmed by the infrared spectrum described in the following paper. Semihydrogenation gave hexa-*trans*-2 : *cis*-4-dienoic acid in fair yield.

Wholly rational routes to hexa-*cis*-2-en-4-yenoic acid seemed unpromising; yet this acid is a close model for a number of natural polyacetylenic esters [Wiljams, Smirnov, and



Golmov, *J. Gen. Chem. (U.S.S.R.)*, 1935, 5, 1195; Sørensen *et al.*, *Acta Chem. Scand.*, 1951, 5, 1244; 1952, 6, 883; 1954, 8, 26], and its omission from the group of acids studied would be unfortunate. The tendency for carbonyl groups in polycyclic systems to facilitate the hydrogenation of adjacent ethylenic linkages (Stavely and Bollenback, *J. Amer. Chem.*

Soc., 1943, 65, 1290; Bladon *et al.*, *J.*, 1953, 2921) suggested, however, that with hexa-2 : 4-dienoic acid the initial attack might be mainly on the Δ^2 -linkage; furthermore studies of the dissociation constants of a number of unsaturated acids showed that *trans*-hex-2-en-4-ynoic acid (pK 4.1) could be separated fairly easily from all $\alpha\beta$ -acetylenic acids (pK 1.6—2.6) and all non-acetylenic acids (pK *ca.* 4.7) by counter-current distribution. This reaction was therefore examined, although it was known (Riley, *J.*, 1953, 2193, and unpublished work from these laboratories) that catalytic hydrogenation of 1 : 3-diacetylenes does not normally give even moderate yields of vinylacetylenes. Counter-current distribution between a phosphate buffer and diisopropyl ether in a 24-tube apparatus, with 100 transfers, resulted in the isolation, at the extremes, of hexa-*cis*-2 : *cis*-4-dienoic acid (20%) and unchanged hexadiynoic acid (30%). In the intermediate tubes two other substances were identified; one, isolated in 0.5% yield, was clearly the desired hex-*cis*-2-en-4-ynoic acid, in view of analytical data and spectroscopic results. The other product (yield 0.2%) appeared from its infrared spectrum to be an unsaturated lactone; it had ultraviolet maxima at 2200 and 3010 Å, which may be compared with λ_{max} . 2980 Å, $\epsilon = 5,000$, quoted by Fried and Elderfield (*J. Org. Chem.* 1941, 6, 566) for 5-methyl- α -pyrone. This substance must almost certainly be 6-methyl- α -pyrone, formed from the *cis*-hexenynoic acid by a cyclisation process subsequent to hydrogenation, probably catalysed by the considerable quantity of hexa-2 : 4-dienoic acid (pK 1.7) still present :



During the course of this work Eisner, Elvidge, and Linstead (*J.*, 1953, 1372) described the preparation of hexa-*cis*-2 : *trans*-4-dienoic acid by the action of sodium ethoxide on the lactone of 4-hydroxyhex-2-enoic acid. This reaction [cf. Jones and Whiting (*J.*, 1949, 143) for the closely analogous preparation of 2-methoxyhexa-2 : 4-dienoic acid] is undoubtedly better than the hydrogenation method described above for *cis*-2 : *trans*-4-dienoic acids.

The melting points of the various hexadienoic and hexenynoic acids (Table 1) clearly reveal the effects of molecular symmetry, in particular in that the *cis-cis*-hexadienoic acid melts much higher than either of the *cis-trans*-isomers. A similar relation has been postulated (Lohaus and Gill, *Annalen*, 1935, 517, 278) in the case of the piperic acids, all four of which are known although their configurations are not securely established. The melting points may directly affect stability in air; the three acids with *m. p.s.* about 30—40° are normally very much less stable than the higher-melting acids, apparently because they deliquesce superficially and are then subject to oxidation in the liquid state. Eisner *et al.* mention that their *cis-trans*-isomer "polymerised during 2—3 hours at room temperature, but much more slowly at 0°, to a clear brittle resin"; while in the absence of moisture we were able to keep this acid for a year at —5° to 0°, or several days at 15°, without significant decomposition. In solution at higher temperatures, however, all four *cis*-acids were unstable, especially in air, and methods for the preparation of derivatives were modified accordingly. Esterification was best effected at 20° in 2% methanolic sulphuric acid; diazomethane appeared to form pyrazolines at rates not negligible relative to ester formation, and gave slightly impure products. Stereomutation was inappreciable with either method, as judged by infrared spectra. The preparation of amides of the *cis*-hexadienoic acids proved difficult, as the several methods all yielded crude products containing the high-melting *trans-trans*-isomer, which could, however, be largely removed by continuous extraction with pentane; it then remained undissolved.

Ultraviolet absorption spectra were determined in 95% ethanol for all the compounds described, and also for *cis*- and *trans*-but-2-enoic and but-2-ynoic acids and their methyl esters (Table 1). Some special precautions used to obtain increased accuracy are described in the Experimental section. It was found that the hexa-2 : 4-dienoic acids fail to obey Beer's law accurately in some regions of the spectra (Table 2), the reason clearly being a difference between the spectra of the anion and of the uncharged molecule, the magnitude of the difference varying considerably from case to case. Such phenomena are common among enolic β -diketones, etc., but have not, as far as is known, been observed with simple

TABLE 1. *Absorption spectra in 95% ethanol.*

Acid	M. p.	Free acid		Methyl ester		Ref.
		λ_{\max} (Å)	$10^{-3} \epsilon$	λ_{\max} (Å)	$10^{-3} \epsilon$	
$\text{CH}_3\text{·CH}^i\text{=CH·CO}_2\text{H}$	71—72°	2030 2460 *	16·0 0·15	2045 2500 *	16·5 0·14	1
$\text{CH}_3\text{·CH}^c\text{=CH·CO}_2\text{H}$	13·5—14·5	2055 2420 *	13·5 0·25	2055 2450 *	14·0 0·25	
$\text{CH}_3\text{·C}\equiv\text{C·CO}_2\text{H}$	76—77	2050 2120 *	6·4 4·2	2055 2120 *	7·2 4·8	
$\text{CH}_3\text{·CH}^i\text{=CH·CH}^i\text{=CH·CO}_2\text{H}$	132—134	2540	26·0	2585	26·5	2
$\text{CH}_3\text{·CH}^c\text{=CH·CH}^i\text{=CH·CO}_2\text{H}$	35—38	2600	22·5	2620	23·5	
$\text{CH}_3\text{·CH}^i\text{=CH·CH}^c\text{=CH·CO}_2\text{H}$	31—34	2570	21·0	2605	21·5	3
$\text{CH}_3\text{·CH}^c\text{=CH·CH}^c\text{=CH·CO}_2\text{H}$	81·5—82·5	2590	20·0	2635	19·0	
$\text{CH}_3\text{·C}\equiv\text{C·CH}^i\text{=CH·CO}_2\text{H}$	182—183·5	2455	16·0	2570	19·0	
$\text{CH}_3\text{·C}\equiv\text{C·CH}^c\text{=CH·CO}_2\text{H}$	114—117·5	2440	11·0	2585	14·0	
$\text{CH}_3\text{·CH}^i\text{=CH·C}\equiv\text{C·CO}_2\text{H}$	130·5—132·5	2470 2830 *	11·5 0·98	2500 2860 *	13·0 1·5	
$\text{CH}_3\text{·CH}^c\text{=CH·C}\equiv\text{C·CO}_2\text{H}$	33—35	2460 2830 *	10·5 0·95	2490 2860 *	11·5 1·0	
$\text{CH}_3\text{·CH}^i\text{=CH·C}\equiv\text{C·CO}_2\text{H}$	118—120	2200 2340 2460 2590 2750	1·1 1·8 3·1 4·1 2·7	2240 2350 2470 2610 2760	1·1 2·1 3·9 5·3 3·7	

* Inflection.

References: (1) Hausser, Kuhn, Smakula, and Hoffer, *Z. phys. Chem.*, 1935, *B*, **29**, 371, give λ_{\max} 2040 Å, $\epsilon = 11,700$, for the acid. (2) For the acid, *idem, ibid.*, give λ_{\max} 2540 Å, $\epsilon = 24,800$, and Eisner *et al. (loc. cit.)* give λ_{\max} 2570 Å, $\epsilon = 27,400$ (and subsidiary bands). (3) Eisner *et al. (loc. cit.)* give λ_{\max} 2570 Å, $\epsilon = 17,000$ (and subsidiary bands) for the acid, and λ_{\max} 2570 Å, $\epsilon = 17,400$ (and subsidiary bands) for the ester.

All these spectra were determined in pure ethanol, in which we find λ_{\max} 2560 Å, $\epsilon = 27,000$, for *trans-trans-hexa-2 : 4-dienoic acid*.

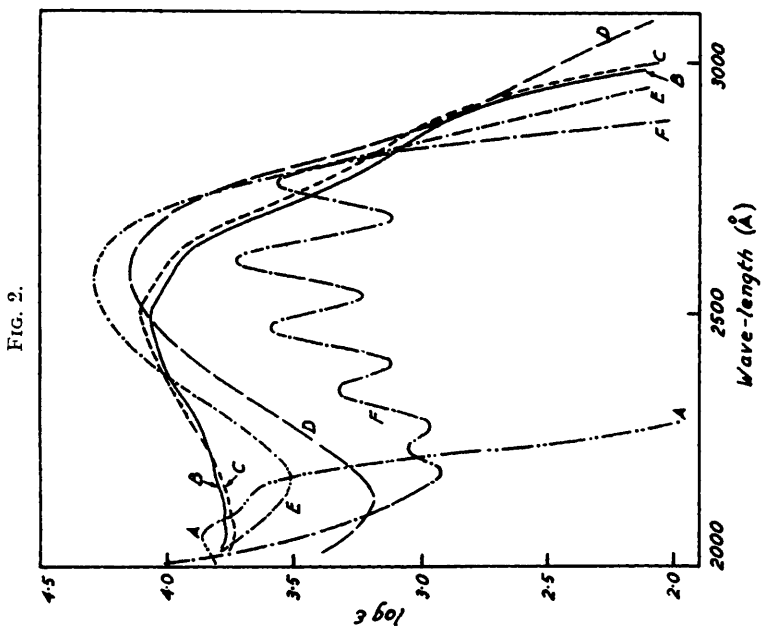
TABLE 2. *Variations of absorption spectra with acidity.*

Acid	Solvent				$10^4 \epsilon$ *
	0·2N-NaOH in 76% EtOH	$10^{-3} \epsilon$	0·2N-H ₂ SO ₄ in 76% EtOH	$10^{-3} \epsilon$	
$\text{CH}_3\text{·CH}^c\text{=CH·CH}^c\text{=CH·CO}_2\text{H}$	2500	17·5	2630	19·5	41·6
$\text{CH}_3\text{·CH}^i\text{=CH·CH}^i\text{=CH·CO}_2\text{H}$	2490	23·5	2585	26·0	37·2
$\text{CH}_3\text{·C}\equiv\text{C·CH}^i\text{=CH·CO}_2\text{H}$	2470	15·5	2540 †	18·5	43·0
$\text{CH}_3\text{·CH}^i\text{=CH·C}\equiv\text{C·CO}_2\text{H}$	2440	11·5	2490	12·5	59·8
$\text{CH}_3\text{·C}\equiv\text{C·C}\equiv\text{C·CO}_2\text{H}$	2320 2440 2560 2720	1·8 2·5 2·55 1·8	2350 2470 2600 2760	2·1 3·6 4·6 3·1	123

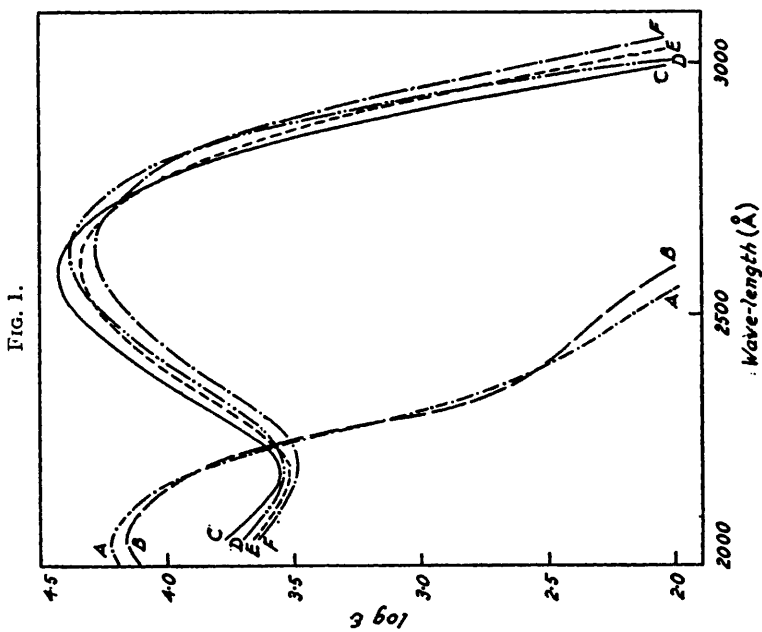
* Concentration (g./100 c.c.) used for these determinations, and for the spectra in 95% ethanol reported in Table 1.

† Value of λ_{\max} unchanged in acidified 95% ethanol.

carboxylic acids before, doubtless because maxima are flat and the shifts small. Curves for the methyl esters are illustrated in Figs. 1 and 2; those obtained for the free acids were similar (Table 1), and need not be discussed in detail. All results obtained for the *trans-trans-* and *cis-2 : trans-4-* acids and their derivatives, however, differ from those reported



A, Methyl but-2-ynoate.
 B, Methyl hex-cis-4-en-2-ynoate.
 C, Methyl hex-cis-4-en-2-ynoate.
 D, Methyl hex-cis-2-en-4-ynoate.
 E, Methyl hex-*trans*-2-en-4-ynoate.
 F, Methyl hexa-2:4-diynoate.



A, Methyl *trans*-but-2-enoate.
 B, Methyl *cis*-but-2-enoate.
 C, Methyl hexa-*trans*-2:4-dienoate.
 D, Methyl hexa-*trans*-2:4-dienoate.
 E, Methyl hexa-*cis*-2:4-dienoate.
 F, Methyl hexa-*cis*-2:4-dienoate.

by Eisner *et al.* (*loc. cit.*) in that in every case only one broad maximum was observed, without subsidiary maxima, inflexions, or even noticeable "shoulders," whereas Eisner *et al.* found groups of two or three maxima in most instances. This discrepancy is not due to the change of solvent (100% instead of 95% ethanol) although intensity readings for sorbic acid in 100% ethanol were a little higher than in 95% ethanol, probably because ionisation was repressed; nor could it be due to lack of resolution in the photoelectric spectrophotometer used here, which easily resolves fine structure closer than that reported. Dr. E. A. Braude has very kindly reinvestigated some of these spectra, using a photoelectric instrument, and also using the original photographic instrument, but with a smaller optical-density interval between match-points, and finds that these "maxima" are unreal. The effect is apparently an optical illusion in reading the plate, connected with the line emission spectrum of the iron arc, and is evidently a danger when compounds with flat maxima are studied by the photographic method. (On the other hand, polyenes and similar substances frequently show genuine subsidiary maxima or inflexions, and casual use of a photoelectric instrument, with readings taken at wide wavelength intervals, might well fail to detect them.) In the case of *trans-trans*-hexa-2:4-dienoic acid the absence of subsidiary maxima or inflexions was finally confirmed by using a recording photoelectric instrument of very high resolving power.

It is believed that the present results for but-2-enoic and but-2-yenoic acids and their esters are more reliable than earlier values. The inflexion at *ca.* 2400 Å in the spectra of but-2-enoic acids and esters is presumably due to a second electronic transition, analogous to that responsible for the weak bands at *ca.* 2100 Å in simple acids (Cason and Sumrell, *J. Org. Chem.*, 1951, 16, 177) and to the well-known band at *ca.* 2700 Å in simple ketones. When two ethylenic bonds are conjugated with the carboxyl group this band becomes submerged just as does the low-intensity carbonyl band in di- and tri-enones. The high-intensity inflexions at *ca.* 2130 Å in the acetylenic compounds, on the other hand, may well be due to partial resolution of vibrational fine structure, as in many vinylacetylenic compounds. The two systems are thus easily distinguished.

The isomeric hexenyenoic esters provide an interesting contrast. The two hex-4-en-2-yenoates show very similar spectra, the fine structure of the *cis*-compound being a little better resolved than that of the *trans*-isomer, just as with the parent pent-3-en-1-yne (Allan and Whiting, *loc. cit.*). The inflexion at *ca.* 2850 Å, $\epsilon = 1200$, is even more prominent in the acids and should be useful diagnostically. The stereoisomeric hex-4-yn-2-enoic esters, on the other hand, differ considerably in intensity, as is very natural when the configuration of the ethylenic bond controls the shape of the chromophore, and neither shows vibrational fine structure. In this latter respect, and in the position and intensity of the absorption maxima of the *trans*-compounds, these isomers resemble the hexa-2:4-dienoic derivatives more closely than do the hex-2-yn-4-enoic derivatives.

The stereoisomeric hexa-2:4-dienoic esters differ appreciably in both λ_{\max} and absorption intensity, the *trans-trans*-isomer absorbing maximally at the *shortest* wavelength, exactly the opposite behaviour to that predicted on the basis of one of Zechmeister's generalisations (*Experientia*, 1954, 10, 1). Naylor and Whiting (*J.*, 1954, 4006) have pointed out that this rule must be inverted for simple, laterally-unsubstituted polyenes. In the present instance it is clear that this result is the consequence of an actual decrease in the electronic energy-level difference on passing from the *trans-trans*- to the *cis-trans*- and then to the *cis-cis*-isomers; it is not a trivial change in the shape of the vibrational band-envelope. This decrease in the energy of the transition accompanies a decrease in its probability; thus Zechmeister's second generalisation, that the all-*trans*-isomer absorbs most strongly, can be applied to these simple polyenes.

Existing theoretical discussions (Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890; Turner and Voitle, *J. Amer. Chem. Soc.*, 1951, 73, 1403) cover the appreciable and variable difference in absorption intensity between the four pairs of esters differing in configuration at the Δ^2 -linkage; in each *cis*-form interference with the coplanarity of the ethylenic linkage and the ester grouping, especially in the preferred *transoid* conformation, may be envisaged, although in the case of hex-*cis*-2-en-4-yenoic ester the influence of the $\text{CH}_3\cdot\text{C}\equiv\text{C}\cdot$ grouping might be predominantly electrostatic, rather than

FIG. 3.

$R \cdot CH=CH \cdot R'$ <i>trans</i>	$R \cdot CH=CH \cdot R'$ <i>cis</i>	$R \cdot CH=CH \cdot CH=CH \cdot R'$ <i>trans</i>	$R \cdot CH=CH \cdot CH=CH \cdot R'$ <i>cis</i>	$R \cdot CH=CH \cdot CH=CH \cdot R'$ <i>trans</i>	$R \cdot CH=CH \cdot CH=CH \cdot R'$ <i>cis</i>	$R \cdot C \equiv C \cdot CH=CH \cdot R'$ <i>cis</i>	$R \cdot C \equiv C \cdot CH=CH \cdot R'$ <i>trans</i>	$R \cdot CH=CH \equiv C \cdot R'$ <i>cis</i>	$R \cdot CH=CH \cdot C \equiv C \cdot R'$ <i>trans</i>	$R \cdot C \equiv C \cdot C \equiv C \cdot R'$	$R \cdot C \equiv C \cdot R'$
-1442 (120) -1432 (100)	-1439 (200) -1413 (150) -1402 (50)	-1432 (160) -1410 (80)	-1444 (180) -1409 (120)	-1441 (160) -1378 (40)	-1442 (180) -1410 (100)	-1433 (120) -1374 (30)	-1433 (140) -1372 (25)	-1434 (160) -1395 (30) -1364 (70)	-1433 (140) -1374 (60)	-1440 (250) -1374 (60)	-1435 (140) -1374 (20)
-1309 (200) -1288 (100) -1261 (180)	-1311 (30) -1281 (60) -1242 (120) -1224 (80) -1194 (600) -1175 (650)	-1324 (500) -1293 (90) -1266 (650) -1242 (80) -1218 (60) -1185 (160)	-1325 (50) -1301 (50) -1271 (70) -1241 (120) -1233 (180) -1194 (700) -1175 (300)	-1346 (70) -1281 (70) -1268 (50) -1226 (300) -1191 (500) -1175 (100)	-1287 (120) -1233 (180) -1218 (140) -1195 (500) -1174 (700)	-1297 (550) -1259 (400) -1193 (160) -1175 (140) -1157 (1100)	-1286 (300) -1250 (800) -1190 (40)	-1256 (700) -1218 (450)	-1286 (300) -1250 (800)	-1293 (1200)	-1253 (1200)
-1101 (80) -1092 (30)	-1092 (30) -1042 (20) -1013 (120) -966 (30)	-1085 (60) -1040 (100) -1015 (80) -995 (350) -943 (60)	-1125 (120) -1040 (90) -1014 (50) -996 (200) -958 (140)	-1123 (80) -1021 (60) -992 (50) -928 (60)	-1118 (90) -1028 (80) -1004 (100) -935 (70)	-1104 (180) -1059 (140) -1012 (70)	-1108 (250) -1096 (460)	-1104 (180)	-1020 (30) -992 (400)	-1072 (450) -1024 (20)	-944 (40)
-832 (40) -812 (160)	-812 (160) -792 (30)	-796 (60) -720 (30)	-832 (180) -803 (80) -758 (50)	-821 (180) -773 (140) -733 (60)	-812 (200) -759 (20) -715 (40)	-789 (20) -714 (40)	-821 (180) -789 (20)	-816 (40)	-822 (90)	-808 (60) -790 (30)	-748 (100)
-682 (30)	-702 (30)	-687 (100)	-662 ()	-662 ()	-668 (30)	-662 ()	-662 ()	-662 ()	-662 ()	-662 ()	-662 ()

The heights of the lines are proportional to the frequency of maxima (cm.⁻¹), given numerically alongside. Figures in parentheses are the corresponding ϵ values. R = CH₃. R' = ·CO₂CH₃.

steric. The *trans* : *cis* intensity ratios for the three pairs of isomers differing at the Δ^4 -linkage, however, are not so easily explained. Whereas the *cis*- and *trans*-forms of penta-1 : 3-diene and pent-3-en-1-yne absorb with practically equal intensity, extension of the chromophore by addition of a methoxycarbonyl group in each case results in an appreciable difference between geometrical isomers, the ratio showing a remarkable consistency (Table 3). Steric inhibition of resonance can be discounted here, since strainless planar

TABLE 3. *Intensity ratios of stereoisomeric esters.*

<i>Differing at Δ^2-linkage.</i>	
<i>trans</i> -But-2-enoic : <i>cis</i> -but-2-enoic	1.18 (± 0.05)
Hexa- <i>trans</i> -2 : <i>trans</i> -4-dienoic : hexa- <i>cis</i> -2 : <i>trans</i> -4-dienoic	1.23 (± 0.02)
Hexa- <i>trans</i> -2 : <i>cis</i> -4-dienoic : hexa- <i>cis</i> -2 : <i>cis</i> -4-dienoic	1.24 (± 0.02)
Hexa- <i>trans</i> -2-en-4-ynoic : hexa- <i>cis</i> -2-en-4-ynoic	1.35 (± 0.03)
<i>Differing at Δ^4-linkage.</i>	
Hexa- <i>trans</i> -2 : <i>trans</i> -4-dienoic : hexa- <i>trans</i> -2 : <i>cis</i> -4-dienoic	1.13 (± 0.02)
Hexa- <i>cis</i> -2 : <i>trans</i> -4-dienoic : hexa- <i>cis</i> -2 : <i>cis</i> -4-dienoic	1.13 (± 0.02)
Hexa- <i>trans</i> -4-en-2-ynoic : hexa- <i>cis</i> -4-en-2-ynoic	1.13 (± 0.02)
<i>trans</i> -Penta-1 : 3-diene : <i>cis</i> -penta-1 : 3-diene	1.02*
<i>trans</i> -Pent-3-en-1-yne : <i>cis</i> -pent-3-en-1-yne	0.97 (± 0.03)†

* Braude and Coles, *J.*, 1951, 2085.† Allan and Whiting, *loc. cit.*

models for every ester can be constructed even when van der Waals radii [which, as Braude *et al.* (*loc. cit.*) have shown, overstate the magnitude of steric interaction] are employed. Apparently other factors—perhaps differential solvation, for example—are involved, although their nature is not yet evident; and the present results accordingly emphasise the need for caution in ascribing to steric hindrance small differences of intensity of absorption between stereoisomers.

Infrared spectra for the acids and esters reported above are discussed in the following paper, in so far as correlation with other related substances is possible. Many bands which cannot yet be assigned should prove useful in recognising the various terminal groupings as complete units, since spectra are probably to a large extent independent of the length of the alkyl groups; this belief was confirmed by examination of Crombie's data. Accordingly, our results for the spectra of the esters in the 660—1450 cm^{-1} region are illustrated in Fig. 3; acids and amides gave generally similar results, with the obvious exceptions of bands attributable to the functional groupings concerned.

EXPERIMENTAL

M. p.s were determined on the Kofler block and are corrected; b. p.s are uncorrected; distillations were effected in the absence of oxygen, refractive indices being constant over at least 3 fractions (except where less than 50 mg. were involved) in cases where no range is quoted. Nitrogen was purified by Fieser's method (*J. Amer. Chem. Soc.*, 1924, **46**, 2639). Low-temperature crystallisations were carried out by gradually cooling solutions from room temperature to -25° (solid carbon dioxide-carbon tetrachloride) or -70° (solid carbon dioxide-acetone), removing the mother-liquors with a pipette, washing with precooled solvent, withdrawn similarly, and finally drying at 20 mm. in a desiccator in a refrigerated room (-5°) in dim light. Ultraviolet absorption spectra were determined, usually in 95% ethanol, with a Unicam S.P. 500 spectrophotometer, a new (life >100 hr.) hydrogen discharge tube being used when the 2000—2050 Å region was examined. The percentage of scattered light (only up to 1% at 2000 Å) was estimated and corrected for by the method of Eglinton, Jones, and Whiting (*J.*, 1952, 2873). Cleanliness of cell faces proved to be extraordinarily important in this region. Cylindrical Hilger cells (1 mm.) were used, and small ($>5\%$) variations in intensity were observed according to their orientation, an arbitrary, but roughly average, position being employed consistently for work at short wavelengths. The precision of the results may be judged by the following replicate values for λ_{max} (Å) and $10^{-3}\epsilon$; *trans*-but-2-enoic acid 2030 (16.0), 2030 (16.1); methyl *cis*-but-2-enoate, 2055 (13.9), 2055 (14.2); hexa-*cis*-2 : *trans*-4-dienoic acid, 2570 (20.8), 2570 (20.9), 2580 (21.3); hexa-*trans*-2 : *cis*-4-dienoic acid, 2600 (22.4), 2600 (22.6);

hexa-*trans*-2 : *trans*-4-dienoic acid, 2540 (26.0), 2540 (25.8); methyl hex-*trans*-4-en-2-ynoate, 2495 (12.7), 2505 (12.8); methyl hex-*trans*-2-en-4-ynoate, 2570 (18.6), 2570 (19.2). These are independent measurements on different samples; there were, however, cases where agreement between duplicate ultraviolet and infrared spectra of crystalline acids was less satisfactory because purification was incomplete, and with these recrystallisation was continued until the results became consistent.

Partial Reduction of Acetylenic Acids. General Method.—The acid, in the appropriate solvent, was shaken in hydrogen with Lindlar's catalyst (*loc. cit.*) (30.0 g. per mole of C≡C) and quinoline (10.0 g. per mole of C≡C), and the reaction was interrupted after the uptake of 1 mol. The acetylenic acid, when insoluble, passed into solution as the hydrogenation proceeded. After addition of ether (*ca.* one-third of the volume of the suspension), the catalyst was filtered off and the filtrate washed with 20% sulphuric acid saturated with potassium hydrogen sulphate (4 × 500 c.c. per mole) and dried (MgSO₄). Evaporation of the solvent at 20 mm. in a stream of nitrogen or carbon dioxide at room temperature afforded the crude acid.

trans-Hex-4-en-2-ynoic acid.—*trans*-Pent-2-en-4-yne (4.0 g.) was converted into an ethereal solution (200 c.c.) of its Grignard derivative which was added to a large excess of powdered carbon dioxide and set aside overnight, moisture being excluded by a "Cellophane" membrane. The resulting complex was decomposed by addition of 2*N*-sulphuric acid (ice), and the aqueous phase saturated with sodium chloride and thoroughly extracted with ether. The acid fraction, isolated *via* *N*-sodium hydroxide, afforded *trans-hex-4-en-2-ynoic acid* (3.3 g., 55%) as needles, m. p. 126—130°, after sublimation at 80—100° (bath temp.)/5 × 10⁻⁵ mm., raised to 130.5—132.5° (sublimes *ca.* 105°) by further recrystallisations from light petroleum (b. p. 80—100°) (Found: C, 65.35; H, 5.1. C₆H₆O₂ requires C, 65.45; H, 5.45%). The *methyl ester* had b. p. 105—110° (bath temp.)/20 mm., *n*_D²⁰ 1.4868—1.4870, m. p. 14—16° (Found: C, 68.15; H, 6.85. C₇H₈O₂ requires C, 67.75; H, 6.45%).

cis-Hex-4-en-2-ynoic Acid.—When the above method was used, *cis*-pent-2-en-4-yne (13.5 g.) gave *cis-hex-4-en-2-ynoic acid* (8.4 g., 37%) as hygroscopic, elongated plates, m. p. 33—35° (uncorr.), after sublimation at 40—50° (bath temp.)/0.05 mm. and several recrystallisations from pentane at -6° (Found: C, 65.75; H, 5.55%). The *methyl ester*, which rapidly became yellow in air, had b. p. 75—80° (bath temp.)/18 mm., *n*_D²⁰ 1.4802—1.4804 (Found: C, 67.75; H, 6.7%).

Propyne (with D. BRD and P. C. WAILES).—Sodamide was prepared from sodium (380 g., 16.5 mole) in liquid ammonia (8 l.). The temperature of the suspension was reduced to -60° and 1 : 2-dichloropropane (565 g., 5 mole) was forced into the stirred mixture by air pressure during 45 min. After a further 30 min. the cooling bath was removed and the ammonia was allowed to evaporate, final traces being removed on a steam-bath. The stirrer gland was then wired gas-tight and the flask was fitted with a gas outlet tube which led successively through two scrubbers containing 2*N*-sulphuric acid (total of 1 l.; containing phenolphthalein), two drying towers (KOH), two traps, each of 500-c.c. capacity and cooled to -60°, and a guard tube (KOH). The residual sodium salt was decomposed by the addition of 2*N*-sulphuric acid (2 l.; forced in by air pressure, slowly at first) during 1 hr., the flask being tipped manually to mix the reactants and control the rate of gas evolution. At this stage the flask and scrubbing solutions became quite hot. The apparatus was finally swept out with a stream of dry nitrogen, and the propyne, nearly all of which was in the first trap, was rapidly transferred to a small dry pre-cooled (-60°) metal cylinder which was finally sealed. The product from two such experiments weighed 346 g. (87%).

Hex-1-en-4-yn-3-ol.—(a) Propyne (40 g.; as above) was passed during 1 hr. into a solution of ethylmagnesium bromide (from 27 g. of magnesium) in ether (300 c.c.) in a flask fitted with an efficient reflux condenser surmounted by a carbon dioxide-acetone cooling finger. The stirred solution was then heated under reflux in a nitrogen atmosphere during 5 hr. and, after cooling, acraldehyde (62 g.; 74 c.c.) in ether (300 c.c.) was added during 2 hr. After the solution had been stirred for a further hour, saturated aqueous ammonium chloride (250 c.c.) was added followed by ice-cold 5% sulphuric acid until the emulsion was dispersed. Isolation and distillation gave the *alcohol* (54 g., 56%), b. p. 84—86°/60 mm., *n*_D¹⁹ 1.4710—1.4697. An analytical sample had *n*_D²⁰ 1.4705 (Found: C, 74.9; H, 8.45. C₆H₈O requires C, 75.0; H, 8.3%). Light absorption: No maximum above 2200 Å with *E*_{1 cm.}^{1%} > 20. The *α-naphthylurethane* formed needles, m. p. 83.5—84.5°, from light petroleum (b. p. 60—80°) (Found: C, 76.9; H, 5.55; N, 5.35. C₁₇H₁₅O₂N requires C, 77.0; H, 5.65; N, 5.3%).

(b) 1 : 2-Dibromopropane (465 g.) was added to a vigorously stirred solution of potassium hydroxide (400 g.) in butanol (900 c.c.) heated under reflux, and the evolved propyne, after being passed through a drying tower (CaCl₂), was bubbled into ethylmagnesium bromide (from 49 g. of

magnesium) in ether (900 c.c.). Subsequent reaction of the Grignard derivative with acraldehyde (102 g.; 122 c.c.) and isolation in the manner described above gave the alcohol (97 g., 45% from the dibromide), b. p. 69—71°/40 mm., n_D^{25} 1.4680—1.4690.

Hex-2-en-4-yn-1-ol.—The above alcohol (42.0 g.) was shaken with sulphuric acid (420 c.c.; 15% w/v) in nitrogen during 44 hr. Isolation of the product with ether and distillation gave the alcohol (27.0 g., 64%), b. p. 82—84°/8 mm., n_D^{25} 1.5022—1.5030. An analytical sample had n_D^{25} 1.5080 (Found: C, 74.8; H, 8.05%). Light absorption: Max., 2250 Å; $\epsilon = 14,000$. The α -naphthylurethane separated from light petroleum (b. p. 80—100°) in fine needles, m. p. 126—128° (Found: C, 77.5; H, 5.8; N, 5.5%).

trans-Hex-2-en-4-ynoic Acid.—Chromic acid solution (167 c.c.; 6N in 12N-sulphuric acid) was added, with stirring and cooling, to hex-2-en-4-yn-1-ol (24.0 g.) during 30 min. at 10—15°. The product was isolated in the usual way *via* N-sodium hydroxide, aqueous solutions being salted out at each stage. *trans-Hex-2-en-4-ynoic acid* (6.7 g., 25%; m. p. 165—175°) was obtained as needles, m. p. 182—183.5°, after several crystallisations from benzene—light petroleum (b. p. 80—100°) and sublimation at 90° (bath temp.)/0.01 mm. (Found: C, 65.2; H, 5.6%). The *methyl ester* had b. p. 70—75°/20 mm., n_D^{25} 1.4991—1.4987, m. p. 21.5—23.5° (Found: C, 67.65; H, 6.45%).

Penta-1:3-diyne.—This method is an improvement on that described by Armitage, Jones, and Whiting (*J.*, 1952, 1993). 1:4-Dichlorobut-2-yne (154 g.) was added during 1 hr. to a suspension of sodamide (from sodium, 89 g.) in liquid ammonia (2 l.) under reflux (carbon dioxide—acetone cooling finger). After 15 min., methyl iodide (177 g.) was added during 1 hr., and the mixture was stirred under reflux for a further 4 hr. Dry ammonium chloride (20 g.) was then added, followed by water (*ca.* 1.5 l.) at a rate such that the boiling ammonia could be condensed. When the reaction had completely subsided, the aqueous ammonia was cautiously extracted with commercial isobutane, and the combined extracts (800 c.c.) were kept at -5° overnight. Hexa-2:4-diyne crystallised and was separated from the solution by decantation. The bulk of the isobutane was removed from the decantate under partial reflux (CO₂-CCl₄) through a 20'' column packed with Dixon gauze rings ($\frac{1}{16}$ '' \times $\frac{1}{16}$ ''), and the remainder through a similarly-packed 6'' column until the head temperature reached 68°. Distillation of the residue at 20°/13 mm. into a cooled trap gave crude penta-1:3-diyne (29 g., 47%), n_D^{25} 1.4648 (Armitage *et al.*, *loc. cit.*, give b. p. 76.5°/742 mm., n_D^{25} 1.4790). The distillation residue was extracted with ether, and the dried (MgSO₄) extract combined with the hexa-2:4-diyne separated earlier. Removal of the ether through a 12'' Fenske column gave a residue which, after crystallisation from pentane at 0° and sublimation at 40° (bath temp.)/17 mm., afforded hexa-2:4-diyne (10.3 g., 11%), m. p. 66—67° (Armitage, Jones, and Whiting, *J.*, 1951, 44, give m. p. 67°). Penta-1:3-diyne cannot be distilled at atmospheric pressure without serious loss by polymerisation, and is more conveniently used without purification.

Hexa-2:4-diyneic Acid (with J. B. ARMITAGE).—Crude penta-1:3-diyne (9.9 g.) was added to ethylmagnesium bromide (from 5 g., 1.4 equiv., of magnesium) in ether (150 c.c.), and the mixture was stirred and heated under reflux in nitrogen for 3 hr. The cooled solution was added to a large excess of powdered carbon dioxide in an autoclave (capacity 1800 c.c.) which was then sealed and kept at 20° overnight. The Grignard complex was decomposed with ice and 3N-sulphuric acid, and the product isolated in the manner usual for a water-soluble acid. *Hexa-2:4-diyneic acid* (11.0 g., 66%), m. p. 118—120°, formed flat needles, slightly yellow, after one crystallisation from benzene; a colourless sample, m. p. 118—120°, was obtained by sublimation at 80—85° (bath temp.)/0.01 mm. (Found: C, 66.35; H, 3.85. C₆H₄O₂ requires C, 66.65; H, 3.7%). The *methyl ester* had b. p. 30°/0.01 mm., n_D^{25} 1.5152—1.5159 (Found: C, 68.4; H, 5.2. C₇H₆O₂ requires C, 68.85; H, 4.9%).

Partial Catalytic Reduction of Hexa-2:4-diyneic Acid.—The acid (3.95 g.) in ethyl acetate (200 c.c.) was hydrogenated by the general method, the reaction being stopped after the uptake of 920 c.c. (1 mol.) of hydrogen at 23°/751 mm. The crude product (3.65 g.), a semi-crystalline yellow oil, was used (3.35 g.) directly for countercurrent partition in a 24-tube apparatus, with 80 c.c. and 40 c.c. of lower and upper phase, respectively, per tube (Craig and Craig, in Weissberger, "Technique in Organic Chemistry," Interscience Inc., New York, 1950, Vol. III, p. 171—311). Preliminary volumetric results showed that the gross partition ratio between diisopropyl ether and m-phosphate buffer (pH 5.6) was 1.5 and these solvents were therefore selected, the ether being redistilled immediately before use. By the "single-withdrawal" technique 100 transfers were made, 77 raffinate fractions (denoted "fractions 1—77" in order of withdrawal) being collected. The contents of the 24 tubes were then isolated by strongly acidifying each aqueous layer, re-equilibrating with the diisopropyl ether, and again extracting the

aqueous layer with fresh ether; the combined ether extracts from each tube are denoted "tubes 1—24," numbering from the end at which the acid mixture was introduced. The absorption spectra in the region 2400—3100 Å, of representative eluted fractions and final upper phases of the tubes were determined, after suitable dilution with purified 95% ethanol, against solvents of the same composition. Relative transmission densities are summarised graphically in Fig. 4.

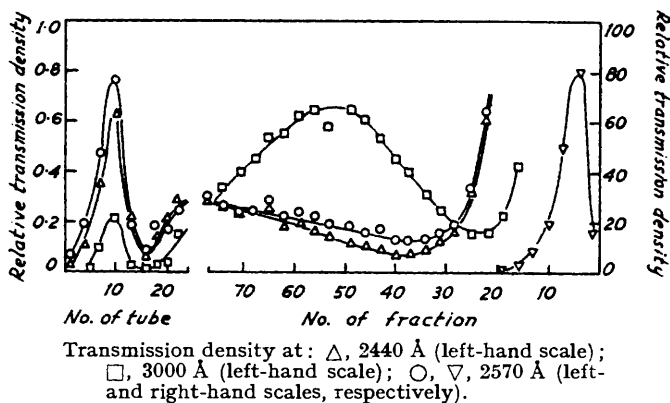
(a) Tubes 1—14 afforded hexa-2:4-dienoic acid (1.21 g., 33%), m. p. and mixed m. p. 116—118°. Tubes 1—4 also contained yellow polymeric material.

(b) Tubes 15—24 and fractions 69—77 afforded, after sublimation at 80—90° (bath temp.)/ 2×10^{-3} mm. and five crystallisations from light petroleum (b. p. 80—100°), *hex-cis-2-en-4-ynoic acid* (19.5 mg., 0.5%), m. p. 114—117.5°, as serrated plates, 5 mm. across (Found: C, 64.95; H, 5.6%). Its melting point and ultraviolet absorption spectrum were unchanged after three further crystallisations.

(c) From the yellow oil, isolated from fractions 60—68, more *cis-hex-2-en-4-ynoic acid* (0.65 mg.), m. p. 111—117°, undepressed on admixture with a sample from (b) above, was obtained after four crystallisations.

(d) The crude material from fractions 30—59 was distilled to give a yellow oil (15 mg.), b. p. 120—125° (bath temp.)/21 mm., n_D^{21} 1.5175, which, after seven recrystallisations from

FIG. 4.



pentane at -60° , afforded 6-methyl- α -pyrone (7.4 mg., 0.2%), m. p. 13—21°, n_D^{21} 1.5175 (Found: C, 65.05; H, 6.35. $C_6H_6O_2$ requires C, 65.45; H, 5.45%). Its infrared spectrum included bands at 1751 cm^{-1} ($\epsilon = 800$), 1644 cm^{-1} ($\epsilon = 160$), and 789 cm^{-1} ($\epsilon = 350$), assigned to C=O stretching, C=C stretching, and *cis*-CH=CH- (conjugated) out-of-plane deformation modes, but lacked those expected for carboxyl groupings.

(e) Fractions 1—29 afforded *cis-cis-hexa-2:4*-dienoic acid (see below) (0.70 g., 19%), m. p. 75—82°, raised to 79—83.5° by further crystallisation, and undepressed on admixture with authentic material. Fractions 1 and 2 also contained yellow polymeric material.

Methyl cis-hex-2-en-4-ynoate.—*cis*-Hex-2-en-4-ynoic acid (11.0 mg.) in dry, freshly distilled ether (2 c.c.) was treated with a dry, freshly distilled ethereal solution of diazomethane (0.74 c.c.; 1.05 equiv.), and the mixture was set aside at 20° for 45 min. Evaporation of the ether and distillation of the residue in an Emich tube gave the ester (8.3 mg., 67%) as a single fraction, b. p. 75—80° (bath temp.)/17 mm., $n_D^{21.5}$ 1.5008 (Found: C, 67.7; H, 6.2%). Unchanged acid (0.70 mg., 6%), which had sublimed subsequently, was recovered and identified by its infrared spectrum.

Hexa-cis-2:trans-4-dienoic Acid.—A suspension of *trans*-hex-4-en-2-ynoic acid (4.00 g.) in purified *n*-hexane (500 c.c.) was partially hydrogenated by the general method; uptake of hydrogen was 910 c.c. at 25°/745 mm. Crystallisations of the crude product from pentane, at -20 and -60° , afforded *hexa-cis-2:trans-4-dienoic acid* (3.10 g., 76%) as needles, m. p. 25—31° (uncorr.), raised to 31—34° (uncorr.) by distillation (b. p. 58—60°/0.05 mm.) and further crystallisation at -60° (Eisner *et al.*, *loc. cit.*, give m. p. 32—35°) (Found: C, 64.65; H, 7.0. Calc. for $C_6H_8O_2$: C, 64.3; H, 7.15%). The methyl ester had b. p. 51—53°/13 mm., n_D^{22} 1.4958 (Eisner *et al.* give b. p. 60°/11 mm., n_D^{22} 1.4948) (Found: C, 66.7; H, 7.95. Calc. for $C_7H_{10}O_2$:

C, 66.65; H, 7.95%). The amide, prepared from the pure acid by the method of Eisner *et al.*, was found to be contaminated with some of the *trans-trans*-isomer. The latter was largely removed by repeated partial sublimation at 50–60° (bath temp.)/0.01 mm. or partial extraction (Soxhlet) with warm pentane, when the higher-melting sorbamide remained unsublimed or undissolved. The desired amide was then crystallised twice from ethyl acetate–light petroleum, giving a product, m. p. 110–116° (Found: C, 64.55; H, 8.1. Calc. for C_6H_9ON : C, 64.85; H, 8.1%). Eisner *et al.* give m. p. 114°; a sample kindly supplied by Dr. J. A. Elvidge had undergone partial decomposition, but after recrystallisation it had m. p. 108–116°, undepressed on admixture with the product obtained as above. Light absorption (our sample): λ_{\max} . 2550 Å; $\epsilon = 22,000$ (Eisner *et al.* give λ_{\max} . 2510 and 2570 Å; $\epsilon = 22,200$).

Hexa-cis-2: cis-4-dienoic Acid and its Derivatives.—*cis*-Hex-4-en-2-ynoic acid (2.40 g.) in purified *n*-hexane (500 cc.) was partially hydrogenated by the general method, the reaction being interrupted when hydrogen absorption became extremely slow, after uptake of 440 c.c. (0.9 mol.) at 25°/762 mm. The crude product was crystallised twice from light petroleum (b. p. 60–80°) affording *cis-cis-hexadienoic acid* (1.28 g., 52%) as flat needles, m. p. 81.5–82.5° (Found: C, 64.3; H, 7.4%). The *methyl ester* had b. p. 80–85° (bath temp.)/20 mm., n_D^{20} 1.4933 (Found: C, 66.4; H, 7.75%). The *amide*, prepared as above, formed needles, m. p. 81–86°, after sublimation at 90–100° (bath temp.)/0.01 mm. and five crystallisations from ethyl acetate–light petroleum (b. p. 60–80°) (Found: C, 64.8; H, 8.4%). Light absorption: λ_{\max} . 2555 Å, $\epsilon = 22,000$.

Hexa-trans-2: cis-4-dienoic Acid.—Hex-*trans*-2-en-4-ynoic acid (3.51 g.), in purified *n*-hexane (400 c.c.) and ethyl acetate (30 c.c.), was partially hydrogenated by the general method, permitted hydrogen uptake being 790 c.c. at 22°/760 mm. A solution of the crude product (2.90 g., 82%) in pentane (*ca.* 7 c.c.) deposited starting material (0.15 g., 4%), m. p. and mixed m. p. 165–176°, when cooled to –4° overnight. Cooling to –60° gave a second crop of crystals which, after distillation [b. p. 60–70° (bath temp.)/0.005 mm.] and four further crystallisations at –60°, afforded *hexa-trans-2: cis-4-dienoic acid* (1.65 g., 46%) as stout needles, m. p. 35–38° (Found: C, 64.0; H, 7.25%). The *methyl ester* had b. p. 85–90° (bath temp.)/20 mm., n_D^{21} 1.5003 (Found: C, 66.95; H, 7.85%). The *amide*, prepared by the above method, was obtained as needles, m. p. 89–93°, after partial sublimation at 80–100° (bath temp.)/0.01 mm., two partial extractions (Soxhlet) with warm pentane, and three crystallisations from ethyl acetate–light petroleum (b. p. 60–80°) (Found: C, 64.75; H, 7.85%). Light absorption: λ_{\max} . 2590 Å; $\epsilon = 24,000$.

cis-But-2-enoic Acid.—A suspension of but-2-ynoic acid (3.03 g.; Henbest, Jones, and Walls, *J.*, 1950, 3646) in purified *n*-hexane (200 c.c.) was partially hydrogenated by the general method. 910 c.c. of hydrogen being absorbed at 22°/751 mm. *cis*-But-2-enoic acid (1.48 g., 48%) formed prisms, m. p. 12.5–14.5°, from pentane at –60°, and had b. p. 70–70.5/17 mm., n_D^{19} 1.4455–1.4458 [Hatch and Nesbit (*J. Amer. Chem. Soc.* 1950, 72, 727) give m. p. 13.5–13.8°, b. p. 54–55°/5 mm., n_D^{20} 1.4450]. The *methyl ester* had b. p. 102–104°/754 mm., n_D^{20} 1.4225 [Burki (*Helv. Chim. Acta*, 1918, 1, 246) gives b. p. 119°] (Found: C, 60.0; H, 8.2. Calc. for $C_5H_8O_2$: C, 60.0; H, 8.0%).

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