1098. *The Preparation of* cis-*Ethylenic Acetylenes by Photoequilibration.*

By J. B. Jones.

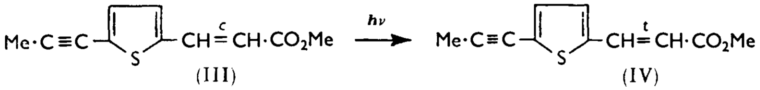
A preliminary survey of the preparation of polyacetylenes containing a *cis*-ethylenic linkage by photoequilibration of the corresponding *trans*-isomer has been carried out. Several *trans*-ethylenic polyacetylenes have been irradiated under varying conditions, and the photoisomerisation products have been analysed.

In a large proportion of the naturally occurring polyacetylenes containing an ethylenic linkage, the double bond has the *cis*-configuration, which considerably multiplies the problems of their synthesis. Starting materials containing a *cis*-double bond are of limited availability, and their purification is generally tedious. Also, the compounds of greatest use, namely, alcohols [1] and acids,[2] readily undergo acid- or base-catalysed cyclisation. The isolation in recent years of further *cis*-ethylenic polyacetylenes [3] added urgency to the problems of increasing the availability of *cis*-ethylenic acetylenes for synthetic purposes. Chemical methods, including dehydration,[4] anionotropic rearrangement of 1-en-4-yn-3-ol systems,[2,5] and stereospecific reduction [6] of a triple bond, did not appear very promising owing to the difficulties mentioned above, and attention was turned towards the photochemical isomerisation of double bonds by visible or ultraviolet light,[7] as *trans*-isomers are relatively readily accessible.

Photochemical *cis–trans* equilibration has been little studied for naturally occurring polyacetylenes. However, the *cis*-ethylenic polyacetylenes (I) and (III) have been photoisomerised to the respective *trans*-isomers (II) [8] and (IV) [9] by Sörensen and his collaborators. Photoequilibration of the ester (I) presumably gave the four possible *cis–trans*-combinations, but only the most readily crystallised isomer (II) was isolated.

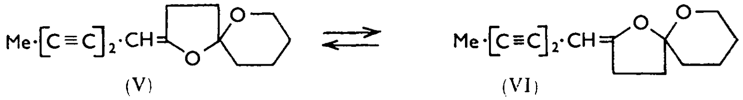
$$CH_3{\cdot}CH\overset{c}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}CH\overset{c}{=}CH{\cdot}CO_2Me \xrightarrow{h\nu} CH_3{\cdot}CH\overset{c}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}CH\overset{t}{=}CH{\cdot}CO_2Me$$

(I) (II)



(III) (IV)

Subsequently to the work described in this paper, further examples were reported by Bohlmann and his co-workers [10] who showed that, for example, compounds (V) and (VI) could be photoequilibrated.



(V) (VI)

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[1] Heilbron, Jones, and Sondheimer, *J.*, 1947, 1586.

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

[3] Jones, *Proc. Chem. Soc.*, 1960, 199; Sörensen, *ibid.*, 1961, 98; Bohlmann, *Chimia* (*Switz.*), 1962, **16**, 353.

[4] Allan and Whiting, *J.*, 1953, 3314.

[5] (*a*) Oroshnik *J. Amer. Chem. Soc.*, 1956, **78**, 2651; (*b*) Bell, Jones, and Whiting, *J.*, 1957, 2597.

[6] Raphael, " Acetylenic Compounds in Organic Syntheses," Butterworths, London, 1955, pp. 22 *et seq.*

[7] Noyes and Boekelheide in " Technique of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, 1948, Vol. II, p. 124; Perkin, *J.*, 1881, **39**, 409.

[8] Sörensen and Stene, *Annalen*, 1941, **549**, 80; Bruun, Christensen, Haag, Stene, and Sörensen, *Acta Chem. Scand.*, 1951, **5**, 1244.

[9] Guddall and Sörensen, *Acta Chem. Scand.*, 1959, **13**, 1185.

[10] Bohlmann, Herbst, and Dohrmann, *Chem. Ber.*, 1963, **96**, 226.

As the primary purpose of the investigation was to determine the broad scope of the method, no attempt was made to use monochromatic radiation. However, the use of soda glass, Pyrex glass, and quartz apparatus, which transmitted light of $\lambda > 3100$, $\lambda > 2900$, and $\lambda > 1950$ Å, respectively, enabled a broad selection of wavelengths to be made. Later, an appraisal of the efficiency of isomerisation in much narrower frequency ranges was envisaged.

Polyacetylenic compounds with fairly extended chromophores, which absorbed at relatively long wavelengths, were selected for the initial studies in order that low energy radiation might be used to raise the compounds to the triplet state,[11] thereby minimising the disruption of the molecules by the higher-energy frequencies. Also, as many functional groups, and certain solvents, *e.g.*, alcohols, participate in photochemical reactions,[12] irradiations were carried out as far as possible in inert solvents and at high dilution. The use of ethers as solvents was precluded by the ease of peroxide formation, which was found to give rise to radicals under the reaction conditions with subsequent attack of the polyacetylenic chain.

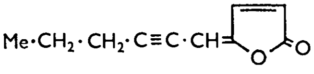
The observation by Sörensen and his co-workers [8] that the double bond adjacent to the ester group in *cis*-matricaria ester (I) was preferentially isomerised during irradiation suggested activation by the methoxycarbonyl group, so a system in which the double bond was conjugated directly with an ester group was studied first.

Lachnophyllum ester, which occurs in Nature as both the *cis*- [13] and the *trans*-isomer,[14] was used for the initial investigation. The *trans*-ester (VII; R = Me), on irradiation in light petroleum in Pyrex glass for one hour at 20°, was converted into the *cis*-ester to the extent of 80%, estimated from the intensity of the new band at 809 cm.^{-1} (*cis*-CH=CH) in the infrared spectrum. Chromatography on alumina afforded the pure *cis*-isomer in 60% yield.

In order to ascertain whether photoequilibration of the acid was as favourable, *trans*-lachnophyllum acid (VII; R = H) was irradiated in benzene under the above conditions for three hours. Isomerisation occurred to the *cis*-acid, which then spontaneously cyclised to the γ-lactone (VIII), the latter being detected by the appearance of infrared bands at

$$\mathrm{Me{\cdot}CH_2{\cdot}CH_2{\cdot}[C{\equiv}C]_2{\cdot}CH\overset{t}{=}CH{\cdot}CO_2R} \qquad \text{(VII)}$$

$$\mathrm{Me{\cdot}CH\overset{t}{=}CH{\cdot}[C{\equiv}C]_2{\cdot}CO_2R} \qquad \text{(IX)}$$



(VIII)

1778 and 819 cm.^{-1}. The overall yield of lactone was estimated spectroscopically to be 30%, and, as its formation defeated the purpose of this investigation, no further attempts were made to photoequilibrate the free acid. After the encouraging results obtained with *trans*-lachnophyllum ester, with the double bond conjugated directly with the ester group, it was of interest to see whether the facilitating effect of the methoxycarbonyl group could be relayed by a polyacetylenic chain.

trans-Oct-6-ene-2,4-diynoic acid (IX; R = H), prepared by Chodkiewicz coupling,[15] was esterified to give the *trans*-methyl ester (IX; R = Me), and, for comparison and in order to determine the ease of separation of a mixture of the *cis*- and *trans*-esters, the *cis*-methyl ester was also prepared. A low yield of the latter was obtained, partly owing to inefficient coupling, which has been observed previously in coupling reactions of some *cis*-ethylenic acetylenes,[16] and partly as a result of the instability of the *cis*-isomer which underwent appreciable decomposition during chromatography. The *cis*-methyl ester could be character-

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[11] Cf. Reid, *Quart. Rev.*, 1958, **12**, 205.

[12] Ref. 7, pp. 112—123.

[13] Wiljams, Smirnov, and Goljmov, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1195; Sörensen *et al.*, *Acta Chem. Scand.*, 1953, **7**, 1375, and earlier papers.

[14] Holme and Sörensen, *Acta Chem. Scand.*, 1954, **8**, 280.

[15] Chodkiewicz, *Ann. Chim.* (*France*), 1957, **2**, 852.

[16] Boehm and Whiting, personal communication.

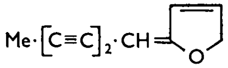
ised only by infrared and quantitative ultraviolet spectroscopy. Mixtures of the *cis*- and the *trans*-isomer were resolved by gas–liquid chromatography, thus providing a convenient method for the quantitative analysis of the products from the irradiation experiments.

The *trans*-ester (IX; R = Me) was irradiated in light petroleum in the Pyrex glass apparatus. The infrared spectrum after irradiation showed a new band at 714 cm.$^{-1}$ (*cis*-CH=CH), and the photoequilibrium mixture was shown by gas–liquid chromatography to contain 45% of the *cis*-ester. Photoequilibration was complete within 15 minutes, the composition of the mixture being unaltered by further irradiation. Owing to the proven instability of the *cis*-ester, its isolation from the photoequilibrium mixture was not attempted.

The experiments described above established the preparation of fully conjugated *cis*-polyacetylenic esters. *trans*-Dec-2-ene-4,6,8-triyn-1-ol (*trans*-dehydromatricarianol) (X) was selected as model for ethylenic systems having acetylenic conjugation only. It was irradiated initially in ethanol (insoluble in light petroleum) in the Pyrex apparatus, but, even though the enetriyne chromophore absorbed strongly in the wavelength range used, no detectable isomerisation occurred during three hours' exposure. However, on irradiation in the quartz apparatus, it underwent partial photoequilibration, which was unfortunately accompanied by considerable disruption of the polyacetylene chain. Chromatography of the mixture on alumina removed the decomposition products (40%), and separated the photoisomerised material into a relatively non-polar component (10%), and a mixture (50%) of the *trans*-alcohol (X) and its *cis*-isomer. The less polar product was shown to be 1,4-epoxydeca-2,4-diene-6,8-diyne (XI), formed by cyclisation under the reaction conditions of some of the *cis*-enetriynol produced. The configuration of the latter facilitates internal attack at C-4. Careful chromatography of the epoxide, during which further decomposition took place, effected a further resolution into two isomers. The isomer eluted first (α; 1·5% overall yield) did not crystallise but was characterised by infrared and quantitative ultraviolet spectroscopy. The other isomer (β; 4% overall yield) crystallised and had essentially the same ultraviolet absorption. The differences in the infrared spectra of the α- and β-compounds could be ascribed to stereoisomerism about the exocyclic double bond in (XI).

$$\mathrm{Me\cdot[C{\equiv}C]_2\cdot C{\equiv}C\cdot CH\overset{t}{=}CH\cdot CH_2\cdot OH}$$

(X)



(XI)

The mixture of *trans*- and *cis*-alcohols obtained as above was analysed by cyclisation of the *cis*-isomer to the epoxide (XI) with base, followed by chromatographic separation from the unchanged *trans*-compound. Estimation in this way showed the *cis*-alcohol to have been formed in 17% overall yield. The infrared and ultraviolet spectra of the cyclised material were identical with those of the β-isomer isolated previously. The base-catalysed cyclisation of the *cis*-alcohol almost certainly involves *trans*-nucleophilic addition to the triple bond,[17] and the β-isomer must therefore have the configuration given in (XII; R = H). The α-isomer is presumably formed by photoisomerisation of the exocyclic double bond in (XII; R = H), and is assigned structure (XIII; R = H). The more extended chromophore of (XII; R = H) is in agreement with the observation that, of the two isomers, the β-compound has the more intense ultraviolet absorption. The β-isomer (XII; R = H) gave the photoequilibrium mixture of the two isomers, α and β, on irradiation in ethanol under the original conditions. In order to substantiate the structural assignments made, a compound containing an authentic example of the chromophore of (XII) was obtained by base-catalysed cyclisation of *cis*-undec-3-ene-5,7,9-triyn-2-ol. *trans*-Nucleophilic addition [17] gave a quantitative yield of the crystalline isomer (XII; R = Me) which had an ultraviolet absorption almost identical with that of the β-isomer obtained from the parent *cis*-alcohol.

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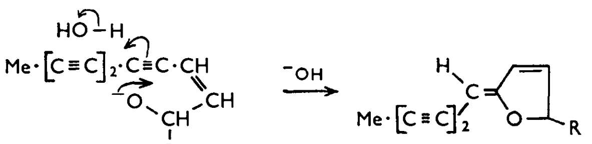
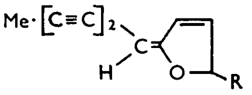
[17] Cf. Truce in "Organic Sulphur Compounds," ed. Kharash, Macmillan, New York, 1961, Vol. I, p. 112.



(XII)



(XIII)

Experiments are in progress to investigate further the scope of the method. Also, refinements of the techniques used are being made by the use of lower-energy monochromatic radiation in conjunction with triplet transfer compounds, *e.g.*, benzophenone.[18]

EXPERIMENTAL

Purified or " spectroscopic " solvents were used in the irradiation experiments. Light petroleum refers to the grade of b. p. 40—60°. Gas–liquid chromatography of the polyacetylenes was carried out on 10% " Apiezon L " on " Embacel " at 200°, with argon as the carrier gas and with β-ray detection. Ultraviolet spectra were determined on a Cary recording spectrophotometer, model 14M, and infrared spectra on a Perkin-Elmer spectrophotometer model 21. Woelm's neutral alumina (activity III) was used for chromatographic separations. M. p.s, which were determined on a Kofler block, are corrected.

Apparatus.—For irradiation with (*a*) $\lambda > 2900$ Å a Pyrex glass container (150 ml.), with a water-cooled finger to maintain the reaction temperature at 20°, was placed 6 in. from a " Hanovia " 500-w quartz, mercury vapour–argon, low-pressure lamp. For work with (*b*) $\lambda > 2000$ Å, a quartz, water-cooled, 500-w " Hanovia Photochemical Reactor " of capacity 250 ml. was used; during irradiation, the temperature of the solution was maintained at 20°.

Methyl trans-*Dec-2-ene-4,6-diynoate* (trans-*Lachnophyllum Ester*) (VII; R = Me).—*trans*-Dec-2-ene-4,6-diynoic acid [19] (100 mg.) in methanol (50 ml.) and concentrated sulphuric acid (1 ml.) was kept for two days in the dark at 20°. Working up in ether, and recrystallisation from pentane at −40°, afforded the *trans*-methyl ester as needles (60 mg.), m. p. 18° (lit., 16—17°,[14] 19° [20]), $\lambda_{max.}$ 2150 (ε 30,500), 2230 (ε 37,700), 2720 (infl.) (ε 12,400), 2870 (ε 22,000), and 3050 Å (ε 22,000), $\nu_{max.}$ (in CS_2) 2223 ($C\equiv C$), 1730 (ester CO), and 952 cm.$^{-1}$ (*trans*-CH=CH).

Irradiation of Methyl trans-*Dec-2-ene-4,6-diynoate*.—The above *trans*-ester (20 mg.) in light petroleum (100 ml.) was irradiated in the Pyrex apparatus for 1 hr. at 20°. Evaporation of the solvent gave an oil which was estimated to consist of 80% of the *cis*-ester from the intensity of the band at 809 cm.$^{-1}$ in the infrared spectrum. Chromatography in light petroleum (3 ml.) in the dark on alumina (5 g.), and elution with the same solvent, gave first a mixture of *trans*- and *cis*-esters, followed by methyl *cis*-dec-2-ene-4,6-diynoate (12 mg.), which recrystallised from pentane at −40° as needles (6 mg.), m. p. 30—31° (lit., 31°,[20] 32·5° [21]), $\lambda_{max.}$ 2160 (ε 20,200), 2240 (ε 26,200), 2750 (infl.) (ε 9600), 2900 (ε 14,400), and 3070 (ε 13,400), $\nu_{max.}$ (in CS_2), 2220 ($C\equiv C$), 1730 and 1715 (ester CO), and 809 cm.$^{-1}$ (*cis*-CH=CH).

Methyl trans-*Oct-6-ene-2,4-diynoate* (IX; R = Me).—*trans*-Bromopent-3-en-1-yne [17] [from *trans*-pent-3-en-1-yne [21] (260 mg.)] in methanol (2 ml.) was added dropwise with stirring under nitrogen at 25° during 10 min. to 33% aqueous ethylamine (6 ml.), cuprous chloride (80 mg.), a crystal of hydroxylamine hydrochloride,[15] and propiolic acid [22] (280 mg.). After the mixture had been stirred for a further 10 min. the acid was isolated by pouring the whole into N-hydrochloric acid and extracting it with ether. This acid was purified by extraction into sodium hydrogen carbonate solution and was re-isolated with ether. Evaporation of the dried ($MgSO_4$) ether solution afforded *trans*-oct-6-ene-2,4-diynoic acid as a solid (500 mg.). Esterification with methanol–sulphuric acid at 20° for 4 days gave the *methyl ester* which separated from pentane as needles (345 mg.), m. p. 34—35° (Found: C, 73·0; H, 5·55. $C_9H_8O_2$ requires C, 72·9; H, 5·5%), $\lambda_{max.}$ 2150 (ε 45,000), 2220 (ε 38,000), 2530 (ε 6500), 2660 (infl.) (ε 9100), 2730 (ε 10,500), 2890 (ε 13,500), 3070 (ε 8800), and 3380 Å (ε 930), $\nu_{max.}$ (in CS_2) 2213 ($C\equiv C$), 1712 (ester CO), 942 (*trans*-CH=CH), and 740 cm.$^{-1}$ ($\equiv C{\cdot}CO_2Me$).

Methyl cis-*Oct-6-ene-2,4-diynoate*.—Methyl *cis*-oct-6-ene-2,4-diynoate was prepared by the method described above for the *trans*-ester, from *cis*-pent-3-en-1-yne [21] (260 mg.) and propiolic

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[18] Cf. Hammond, Leermakers, and Turro, *J. Amer. Chem. Soc.*, 1961, **83**, 2396.

[19] Bell, Jones, and Whiting, *J.*, 1958, 1313.

[20] Bruun, Haag, and Sörensen, *Acta Chem. Scand.*, 1950, **4**, 850.

[21] Eglinton and Whiting, *J.*, 1950, 3650.

[22] Wolf, *Chem. Ber.*, 1953, **86**, 735.

acid [22] (280 mg.). The crude product obtained from the esterification was purified by chromatography in light petroleum in the dark on alumina (30 g.). Elution with the same solvent afforded the *cis*-methyl ester as an unstable viscous oil (40 mg.) which was shown to be pure by gas–liquid chromatography and by infrared and ultraviolet absorption spectroscopy: $\lambda_{\text{max.}}$ 2530 (ε 4500), 2600 (infl.) (ε 5000), 2730 (ε 7300), 2880 (ε 10,100), 3060 (ε 6400), and 3370 Å (ε 530), $\nu_{\text{max.}}$ (in CS_2) 2200 (C≡C), 1712 (ester CO), 740 (≡C–CO_2Me), and 714 (*cis*-CH=CH).

Irradiation of Methyl trans-*Oct*-6-*ene*-2,4-*diynoate* (IX; R = Me).—The *trans*-ester (20 mg.) in light petroleum (100 ml.) was irradiated at 20° in the Pyrex apparatus, and the extent of isomerisation was estimated at intervals by gas–liquid chromatography. The mixture after 15 minutes' exposure was found to contain 45% of the *cis*-ester. The composition was unchanged by further irradiation. The above estimation of the percentage composition of *cis*- and *trans*-esters in the photoequilibrium mixture was confirmed by the relative intensities of the characteristic bands in the infrared spectrum.

trans-*Dec*-2-*ene*-4,6,8-*triyn*-1-*ol* (trans-*Dehydromatricarianol*) (X).—1-Bromopenta-1,3-diyne [15] (from penta-1,3-diyne,[23] 350 mg.) in methanol (2 ml.) was coupled under Chodkiewicz conditions [15] with *trans*-pent-2-en-4-yn-1-ol [24] (410 mg.), and the crude alcohol (586 mg.) was rigorously purified by chromatography on alumina (100 g.). Elution with benzene–light petroleum (1 : 50) gave *trans*-dec-2-ene-4,6,8-triyn-1-ol, which crystallised from ether–pentane as rhombs (450 mg.), m. p. 129° (lit.,[15,25] 129°), $\lambda_{\text{max.}}$ 2110 (ε 44,400), 2225 (infl.) (ε 55,400), 2330 (ε 90,000), 2420 (ε 108,000), 2570 (ε 3500), 2710 (ε 6500), 2890 (ε 12,400), 3075 (ε 16,300), and 3290 Å (ε 11,200), $\nu_{\text{max.}}$ (in CS_2) 3550 (OH), 2210 (C≡C), and 942 cm.$^{-1}$ (*trans*-CH=CH).

Irradiation of trans-*Dec*-2-*ene*-4,6,8-*triyn*-1-*ol*.—The above *trans*-alcohol (210 mg.) in ethanol (250 ml.) was irradiated for 45 min. in the quartz apparatus. The resulting brown solution was evaporated in nitrogen, and the residue was chromatographed in the dark on alumina (40 g.). Elution with light petroleum afforded 1,4-epoxydeca-2,4-diene-6,8-diyne (XI) (20 mg.), and subsequent elution with benzene–light petroleum (1 : 50) gave dec-2-ene-4,6,8-triyn-1-ol (105 mg.), shown to be a mixture of the *cis*- and *trans*-isomers by the infrared absorption at 942 (*trans*-CH=CH) and 730 cm.$^{-1}$ (*cis*-CH=CH).

The 1,4-epoxydeca-2,4-diene-6,8-diyne was rechromatographed in light petroleum in the dark on alumina (5 g.). Elution with the same solvent gave first the α-isomer (XIII; R = H) (3·2 mg.), $\lambda_{\text{max.}}$ 2290 (ε 6500), 2390 (ε 6600), 2520 (ε 3700), 2660 (ε 3800), and 3175 Å (ε 11,500), $\nu_{\text{max.}}$ (in CCl_4 and CS_2) 1627 (C=C·O), 1165 (=C·O·), 777 (*cis*-CH=CH, cyclic), and 745 and 711 cm.$^{-1}$ (CH=CR_2), followed by the β-isomer (XII; R = H) (8·2 mg.) (properties given below).

The *cis*- and *trans*-enetriynol mixture (105 mg.), obtained as above, was kept in 0·1N-potassium hydroxide (30 ml., 50% aqueous ethanolic) at 20° for 1 hr. Water (200 ml.) was added, the aqueous solution was extracted with ether (2 × 50 ml.), and the ethereal extracts were dried ($MgSO_4$) and evaporated. Chromatography of the residue as described above gave β-1,4-*epoxydeca*-2,4-*diene*-6,8-*diyne* (XII; R = H) (36 mg.), eluted with light petroleum, and *trans*-dec-2-ene-4,6,8-triyn-1-ol (67 mg.), eluted with benzene–light petroleum (1 : 50). The β-compound recrystallised from ether–pentane at −40° as prismatic needles (30 mg.), m. p. 78° (Found: C, 83·35; H, 5·6. $C_{10}H_8O$ requires C, 83·3; H, 5·6%), $\lambda_{\text{max.}}$ 2300 (ε 8200), 2375 (ε 8900), 2535 (ε 4000), 2670 (ε 6400), and 3170 Å (ε 21,000), $\nu_{\text{max.}}$ (in CCl_4 and CS_2) 1627 (C=C·O), 1156 (=C·O·), 887 (β-CH=CR_2), and 768 cm.$^{-1}$ (*cis*-CH=CH, cyclic).

cis-*Undec*-3-*ene*-5,7,9-*triyn*-2-*ol*.—*cis*-Hex-3-en-5-yn-2-ol [5b] (48 mg.) was mixed with 33% aqueous ethylamine (0·4 ml.), cuprous chloride (10 mg.), and a crystal of hydroxylamine hydrochloride.[15] 1-Bromopenta-1,3-diyne [15] [from penta-1,3-diyne,[23] (35 mg.)] in methanol (0·2 ml.) was added dropwise during 10 min., with stirring under nitrogen, at 30°. After a further 10 minutes' stirring, the product was isolated through N-hydrochloric acid and ether. The solid obtained was chromatographed in the dark on alumina (5 g.). Benzene-elution gave cis-*undec*-3-*ene*-5,7,9-*triyn*-2-*ol* (62 mg.) which separated from ether–pentane as very light-sensitive, colourless rods (50 mg.), m. p. 87° (Found: C, 83·0; H, 6·65. $C_{11}H_{10}O$ requires C, 83·5; H, 6·4%), $\lambda_{\text{max.}}$ 2100 (ε 36,000), 2300 (ε 65,000), 2420 (ε 112,000) 2570 (ε 3300), 2720 (ε 6500), 2890 (ε 11,800), 3080 (ε 15,600), and 3290 Å (ε 10,800), $\nu_{\text{max.}}$ (in CCl_4 and CS_2), 3550 (OH), 2215 (C≡C), and 750 cm.$^{-1}$ (*cis*-CH=CH).

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[23] Jones, Jones, Skatteböl, and Whiting, *J.*, 1960, 3489.
[24] Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1583.
[25] Gardner, Jones, Leeming, and Stephenson, *J.*, 1960, 691.

2,5-*Epoxyundeca*-3,5-*diene*-7,9-*diyne* (XII; R = Me).—The preceding *cis*-alcohol (20 mg.) in ethanol (5 ml.) and 0·2N-aqueous potassium hydroxide (1 ml.) were kept at 20° for 1 hr. Water (20 ml.) was then added, the solution was extracted with ether (2 × 30 ml.), and the combined extracts were washed with water (30 ml.) and dried ($MgSO_4$). Evaporation of the ether afforded a solid which on recrystallisation from pentane at $-40°$ gave 2,5-*epoxyundeca*-3,5-*diene*-7,9-*diyne* as needles (16 mg.), m. p. 47° (Found: C, 83·5; H, 6·5. $C_{11}H_{10}O$ requires C, 83·5; H, 6·4%), $\lambda_{max.}$ 2095 (ε 14,600), 2175 (infl.) (ε 12,400), 2310 (ε 8500), 2380 (ε 9300), 2540 (ε 4000), 2860 (ε 5100), and 3175 Å (ε 22,600), $\nu_{max.}$ (in CCl_4 and CS_2) 1630 (C=C·O), 1162 (C=C·O), 956 (β-CH=CR_2), and 781 cm.$^{-1}$ (*cis*-CH=CH, cyclic).

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