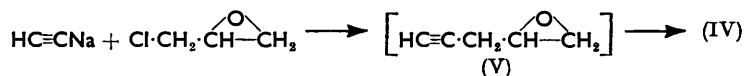


even a 2% content of the *cis*-form would have made this the preferred route. It seems unlikely that the ring-opening of the postulated intermediate (V) would be stereospecific; more probably the *cis*- and the *trans*-form of the alcohol (IV) are both formed, but the former undergoes further reactions (*e.g.*, cyclisation) and is lost.



In a re-examination of the earlier route it was first found that the addition of calcium chloride improved the yield of the chloride mixture from pent-1-en-4-yn-3-ol. In this case fractionation gave not only the *cis*- and the *trans*-conjugated chloride but also some 3-chloropent-1-en-4-yne, readily distinguished by its lack of ultraviolet absorption. The method originally used,⁴ *i.e.*, treatment with potassium acetate in methanol, followed by alcoholic potassium hydroxide, proved best for hydrolysing both the conjugated chlorides to the corresponding alcohols. *cis*-Pent-2-en-4-yn-1-ol was finally obtained, after some attention to improving the methods used, in 1.5% overall yield from acraldehyde.

Since the completion of this work Oroshnik⁷ has stated that in the rearrangement of 3-methylpent-1-en-4-yn-3-ol *cis*- and *trans*-isomers are formed in comparable quantities, the *cis*-isomer actually predominating. In the three rearrangements discussed above, all leading to a system R·CH=CH·C≡CH as against R·CH=CMe·C≡CH in the case described by Oroshnik, the proportion of *cis*-isomer was constant at 20—25%. The considerable difference between the boiling-points of the stereoisomers of vinylacetylenes (7° for the pent-2-en-4-yne,⁸ as against 0.8° for the penta-1 : 3-dienes) is both interesting theoretically and useful synthetically.

Ultraviolet absorption maxima, all obtained with the same instrument, are tabulated below. The intensity data for the very volatile pent-2-en-4-yne (rather lower than those reported earlier⁸) are less accurate than those for the other compounds, but the *cis/trans* ratio is near unity, in agreement with the earlier results (any error will probably be negative, since the *cis*-isomer is the more volatile). The appreciable reduction in the *cis/trans* intensity ratio as the group R in R·CH=CH·C≡CH increases in size cannot in this case imply

Absorption maxima in ethanol of R·CHX·CH=CR'·C≡CH.

R	X	R	<i>cis</i> λ (10 ⁻³ ε)	<i>trans</i> λ 10 ⁻³ ε)	ε _{cis} /ε _{trans}
H	H	H	2215 (11.8)	2225 (12.1)	0.98
H	OH	H	2230 (11.2)	2230 (12.6)	0.89
Me	OH	H	2220 (11.7)	2230 (14.0)	0.84
H	Cl	H	2270 (11.8)	2270 (14.0)	0.84
Me	Cl	H	2255 (12.4)	2265 (15.1)	0.82
H	OH	Me	2230 (11.0)	2240 (13.1)	0.84 ⁷

steric hindrance to the coplanarity of the conjugated system, since the *cis*-isomer has a constant intensity of *ca.* 11,500, while those of the *trans*-isomers vary between 12,000 and 15,000. Rather it is the *trans*-form which shows greater sensitivity to hyperconjugative auxochromes, similar to that observed in the diacetylenes,⁹ where steric considerations are not relevant. Our results, incidentally, support Oroshnik's assignment of configuration to the isomers of 3-methylpent-2-en-4-yn-1-ol.

In all cases the resolution of vibrational fine structure, though slight, was more perceptible in the *cis*- than in the *trans*-isomers.

The infrared spectra of most of these compounds have already been discussed.¹⁰ The *cis*-compounds R·CH=CH·C≡CH, where R = CH₃, HO·CH₂, and ClCH₂, show a curious anomaly in the intensity of the C-H out-of-plane deformation band, which occurs at

⁷ Oroshnik *J. Amer. Chem. Soc.*, 1956, **78**, 2651.

⁸ Allan and Whiting, *J.*, 1953, 3314.

⁹ Armitage and Whiting, *J.*, 1952, 2005.

¹⁰ Allan, Meakins, and Whiting, *J.*, 1955, 1874.

723, 734, and 768 cm^{-1} , respectively: ϵ values, under comparable conditions, are 115, 30, and 150, as compared with values of 140, 130, and 150 for the corresponding *trans*-isomers at 956, 952, and 950 cm^{-1} . The weak band of the *cis*-alcohol is abnormally broad; similar results are consistently obtained for other compounds $\text{R}\cdot\text{CH}=\text{CH}\cdot\text{C}\equiv\text{C}\cdot$ where R is $\text{HO}\cdot\text{CH}_2$ or (to a lesser extent) $\text{CH}_3\cdot\text{CH}(\text{OH})$.

EXPERIMENTAL

Hex-3-en-5-yn-2-ol (II).—Hex-4-en-1-yn-3-ol (120 g.) was stirred with a solution of toluene-*p*-sulphonic acid (40 g.) in water (400 c.c.) at 35° for 24 hr. The initially homogeneous liquid separated into two phases; the product was isolated with ether and distilled, giving a mixture of isomers (102 g., 85%), b. p. 64—71°/14 mm., n_D^{20} 1.4792—1.4850.

This mixture was distilled at about 18 mm. pressure through a column (50 \times 1.4 cm.) packed with 1/16 in. stainless steel rings, a total-condensation still-head set to give a reflux ratio of about 40 : 1 being used. After pre-flooding and heating under reflux for 1 hr., fractions were collected and grouped as follows: (a), b. p. 65.5°, n_D^{24} 1.4736—1.4744 (20.6 g.); (b), b. p. 65.5—76°, n_D^{24} 1.4772, n_D^{20} 1.4830 (9.7 g.); (c), b. p. 76°, n_D^{20} 1.4850—1.4858 (52.5 g.). Fractions (a) were the essentially pure *cis*-isomer, and were redistilled through a column (15 \times 0.7 cm.) packed with similar rings to give the pure *cis*-alcohol, n_D^{21} 1.4758 (Found: C, 74.75; H, 8.5. $\text{C}_6\text{H}_8\text{O}$ requires C, 74.95; H, 8.4%). Similarly redistilled, the pure *trans*-isomer (c) had n_D^{21} 1.4848 (Heilbron, Jones, Smith, and Weedon³ give b. p. 97—81°/30 mm., $n_D^{18.5}$ 1.4842).

The *cis*-alcohol formed a *p*-phenylazobenzoate, prepared by Mills's method,¹¹ which formed plates, m. p. 77—78°, from light petroleum (b. p. 40—60°) (Found: C, 75.1; H, 5.35. $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_2$ requires C, 75.0; H, 5.3%). The same derivative of the *trans*-alcohol formed plates, m. p. 99.5—100.5° (Found: C, 75.2; H, 5.15%).

2-Chlorohex-3-en-5-yne.—Hex-4-en-1-yn-3-ol (200 g.) and concentrated hydrochloric acid (600 c.c.; *d* 1.16) were shaken mechanically in nitrogen at 18° for 30 min. An equal volume of water was added, and the product was isolated with ether and distilled; it had b. p. 59—70°/70 mm., n_D^{21} 1.4740—1.4858 (202 g., 85%).

The mixture of isomers was fractionally distilled. The column already used for the alcohols was employed with a total-condensation still-head equipped with a magnetically-operated 0.5-c.c. bucket; since a reflux meter permitted measurement of the total boil-up rate, the reflux ratio could be precisely determined. A manostat was used to maintain a pressure of 58—59 mm. After pre-flooding and heating under total reflux for 2 hr. the boil-up and take-off rates were adjusted to 420 and 10 c.c./hr., respectively. The fractions obtained were grouped as follows: (a) b. p. 51.8—52.7°, $n_D^{16.5}$ 1.4750—1.4752 (39.8 g.); (b) b. p. 52.7—64.0°, $n_D^{16.5}$ 1.4764—1.4862 (22.6 g.); and (c) b. p. 64.0°, $n_D^{16.5}$ 1.4868 (9.3 g.). Distillation was then interrupted, the column was washed with a little ether, and the washings and still-residue were distilled through a short Vigreux column to give fraction (d), b. p. 63—64°/57 mm., $n_D^{16.5}$ 1.4868—1.4870 (101.4 g.). The pure *cis*-isomer (a) had n_D^{20} 1.4732 (Found: C, 62.95; H, 5.85; Cl, 30.9. $\text{C}_6\text{H}_7\text{Cl}$ requires C, 62.9; H, 6.15; Cl, 30.95%); the *trans*-isomer (c and d; total yield 110.7 g.) had n_D^{21} 1.4850 (Found: C, 63.25; H, 6.1%). Unlike the pent-2-en-4-yne, the chlorohexenyne did not undergo rapid alteration in air at room temperature, the refractive indices remaining constant during 12 hr; however they did darken slowly, and were best stored at -5° in the presence of quinol.

1-Chloropent-2-en-4-yne and *3-Chloropent-1-en-4-yne*.—Pent-1-en-4-yn-3-ol (125 g.) was added to a solution of anhydrous calcium chloride (167 g.) in concentrated hydrochloric acid (600 c.c.) at 18°, and the mixture was shaken mechanically for 30 min. at 18°. Isolation with ether, removal of the solvent through a 20-cm. Widmer column under partial reflux, and distillation gave the mixed isomers (104 g., 70%), b. p. 70°/82 mm.—79°/40 mm., $n_D^{17.5}$ 1.4510—1.4962.

For fractional distillation the apparatus and technique described for hex-3-en-5-yn-2-ol were employed, with a pressure of 134 mm. The fractions collected may be grouped as follows: (a), b. p. 48—50°, n_D^{19} 1.4538 (4.7 g.); (b), b. p. 50°, n_D^{19} 1.4570 (14.5 g.); (c), b. p. 50—65.5°, n_D^{19} 1.4650—1.4832 (9.4 g.); (d), b. p. 65.5°, n_D^{19} 1.4870—1.4874 (13.1 g.); (e), b. p. 65.5—75°, n_D^{19} 1.4904 (4.9 g.); (f), b. p. 75—76°, n_D^{19} 1.4960—1.4968 (10.3 g.). Distillation of the still residues

¹¹ Mills, J., 1951, 2332.

gave additional material (27 g.) (*h*), b. p. 65—67°/89 mm., n_D^{20} 1.4968—1.4972. Of these, fraction (*b*) was 3-chloropent-1-en-4-yne, and after redistillation had n_D^{19} 1.4570 (Found : C, 60.2; H, 5.25. C_6H_5Cl requires C, 59.7; H, 5.0%); fraction (*d*) was *cis*-1-chloropent-2-en-4-yne, and after redistillation had n_D^{19} 1.4870 (Found : C, 59.8; H, 5.05%); and fractions (*f*) and (*h*) were essentially pure *trans*-1-chloropent-2-en-4-yne (Found : C, 59.45; H, 5.1%). The *trans*-chloride contained a trace (*ca.* 1%) of the *cis*-form, according to infrared measurements.

trans-1-Chloropent-2-en-4-yne (preparative method; with J. L. H. ALLAN).—*trans*-Pent-2-en-4-yn-1-ol (10.0 g.) was added dropwise with cooling and stirring to a mixture of pyridine (9.6 g.) and thionyl chloride (21.8 g., 13.1 c.c.) at 0—10°. After being stirred for 18 hr. at 20° the product was poured on ice, and the neutral fraction was isolated with ether. Evaporation of the ether through a 12 in. Fenske column, rapid distillation of the black residue at *ca.* 20°/0.05 mm. into a trap cooled to -80°, and redistillation afforded the *trans*-chloride (6.7 g.), n_D^{19} 1.4982, with an infrared spectrum identical, except for the absence in this case of the band at 768 cm^{-1} (due to a trace of *cis*-isomer), with that of the specimen described above.

cis-Pent-2-en-4-yn-1-ol.—*cis*-1-Chloropent-2-en-4-yne (16.0 g.) was added to a solution of anhydrous potassium acetate (37.5 g.) in methanol (120 c.c.), and the mixture was heated under reflux for 20 hr., potassium chloride separating. Potassium hydroxide (9 g.) was added to the cooled mixture which was stirred to effect solution. After 24 hr. at 20° ether was added and the precipitate was filtered off and washed with ether; the resultant solution was carefully made neutral (phenolphthalein) by addition of *ca.* 2 c.c. of 10% phosphoric acid. The ethereal solution was dried thoroughly ($MgSO_4$), then concentrated through a 20-cm. Widmer column under partial reflux. Distillation of the residue gave *cis*-pent-2-en-4-yl-1-ol (5.85 g.), b. p. 68—69°/19 mm., $n_D^{20.5}$ 1.4870—1.4880. An analytical specimen had $n_D^{21.5}$ 1.4882 (Found : C, 72.7; H, 7.4. C_6H_6O requires C, 73.15; H, 7.35%). It could be kept for months at -18° to -40°, and indeed seemed more stable than the *trans*-isomer. The *p*-phenylazobenzoate formed plates, m. p. 83.5—84.5°, from light petroleum (b. p. 40—60°) (Found : C, 74.55; H, 5.05. $C_{18}H_{14}O_2N_2$ requires C, 74.5; H, 4.85%). The same *derivative* of the *trans*-alcohol had m. p. 102—103° (Found : C, 74.3; H, 4.8%).

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