Researches on Acetylenic Compounds. Part LVI.* The **505**. Stereochemical Consequences of Some Anionotropic Rearrangements.

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In the anionotropic rearrangement of hex-4-en-1-yn-3-ol (" propenylethynylcarbinol") a mixture of the cis- and the trans-isomer is formed. Similar results in the allylic replacement of a hydroxyl group by chlorine permit the preparation of cis-pent-2-en-4-yn-1-ol.

THE rearrangement of hex-4-en-1-yn-3-ol (I) to hex-3-en-5-yn-2-ol (II)¹ has been extensively studied from a mechanistic standpoint.² Careful fractionation, however, has now revealed that the product is a mixture of two alcohols with boiling points differing by 10.5° ; and spectroscopic evidence proves that these are the *cis*- and the *trans*-isomer of (II). Their formation is not related to stereoisomerism in the starting material, which was found to be homogeneous (and trans) by infrared examination of the first and the last fraction after rigorous fractional distillation.

$$\begin{array}{c} \mathsf{CH}_{\mathtt{s}} \cdot \mathsf{CHCI} \cdot \mathsf{CH} = \mathsf{CH} \cdot \mathsf{C} = \mathsf{CH} \xrightarrow{\mathsf{H}^+, \ \mathsf{CI}^-} \mathsf{CH}_{\mathtt{s}} \cdot \mathsf{CH} = \mathsf{CH} \cdot \mathsf{CH}(\mathsf{OH}) \cdot \mathsf{C} = \mathsf{CH} \xrightarrow{\mathsf{H}^+, \ \mathsf{H}_{\mathtt{s}}\mathsf{O}} \mathsf{CH}_{\mathtt{s}} \cdot \mathsf{CH}(\mathsf{OH}) \cdot \mathsf{CH} = \mathsf{CH} \cdot \mathsf{C} = \mathsf{CH} \\ (\mathrm{III}) & (\mathrm{II}) & (\mathrm{III}) \end{array}$$

The heterogeneity of alcohol (II) probably escaped earlier detection through the assumption that the lower-boiling fractions rich in the cis-isomer contained unchanged hex-4-en-1-yn-3-ol (I). In fact, the boiling-point of cis-(II) is near to that of the unconjugated isomer (I), and each has a refractive index lower than that of trans-(II). A mixture of all three isomers cannot conveniently be separated by distillation; a method of isomerisation utilising toluene-p-sulphonic acid which provides an (initially) homogeneous reaction mixture is preferable to the earlier steam-distillation technique.³ The refractive index quoted³ for hex-3-en-5-yn-2-ol (II) implies a trans-content of roughly 80%, whereas the total isomerisation product (yield 85%) is estimated to contain 75-78%of the trans-alcohol. On the other hand, the α -naphthylurethane and 3:5-dinitrobenzoate 1 were clearly those of the *trans*-isomer; these derivatives of the *cis*-alcohol could not be induced to crystallise. Both isomers gave crystalline p-phenylazobenzoates.

When the cis-alcohol (II) was treated with 10% aqueous toluene-p-sulphonic acid at 35° , as in the isometrisation of (I), it was recovered in good (>75%) yield and shown, by infrared examination, to be free from the trans-isomer. Thus the proportions of the two forms are determined by kinetic, rather than thermodynamic, factors.

Treatment of hex-4-en-1-yn-3-ol with concentrated hydrochloric acid gives the corresponding rearranged chloride (III); 4 this also proved to be a mixture of the cis- and the trans-form (b. p. difference 12°).

Pent-2-en-4-yn-1-ol (IV) was first prepared by the rearrangement-chlorination reaction, followed by hydrolysis⁴ (the unconjugated alcohol is rearranged at a negligible rate in H,C=CH·CH(OH)·C=CH → H,C=CH·CHCI·C=CH + CI·CH₃·CH=CH·C=CH → HO·CH₃CH=CH·C=CH (IV)

the absence of chloride ions 4, 2). Subsequently, and much more conveniently, it was obtained by the action of sodium acetylide on epichlorohydrin.⁵ Careful fractionation revealed that when thus prepared, the alcohol contains less than 0.1% of the *cis*-isomer; ⁶ an unfortunate result, since cis-pent-2-en-4-yn-1-ol was a most desirable intermediate, and

- ² Braude and his co-workers, J., 1944, 436, 443; 1946, 122, 128, 396; 1947, 1096; 1948, 794, 1982.
 ³ Heilbron, Jones, Smith, and Weedon, J., 1946, 54.
 ⁴ Heilbron, Jones, Lacey, McCombie, and Raphael, J., 1945, 77.

- ⁵ Haynes, Heilbron, Jones, and Sondheimer, J., 1947, 1583.
- ⁶ Schlögl, unpublished work.

^{*} Part LV, J., 1957, 2012.

¹ Jones and McCombie, J, 1943, 261.

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.

$$HC = CN_{2} + CI \cdot CH_{2} \cdot CH - CH_{2} \longrightarrow \begin{bmatrix} HC = C \cdot CH_{2} \cdot CH - CH_{2} \end{bmatrix} \longrightarrow (IV)$$
(V)

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, 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 Oroshnik ⁷ 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-ynes,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-ynes (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

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R	x	R	<i>cis</i> λ (10 ⁻³ ε)	trans λ 10 ^{-s} ε)	Ecis Etrans
н	н	н	2215 (11.8)	2225 (12.1)	0.98
н	OH	н	2230 (11·2)	2230 (12·6)	0.89
Me	OH	н	2220 (11·7)	2230 (14·0)	0.84
н	Cl	н	2270 (11·8)	2270 (14·0)	0.84
Me	Cl	н	$2255(12\cdot 4)$	2265 (15·1)	0.82
н	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 $R = CH_3$, 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 R•CH=CH•C=C• where R is HO•CH₂ or (to a lesser extent) CH₃•CH(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., $n_{\rm p}^{20}$ 1·4792—1·4850.

This mixture was distilled at about 18 mm. pressure through a column $(50 \times 1.4 \text{ cm.})$ 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. $65 \cdot 5^{\circ}$, n_2^{b} 1.4736—1.4744 (20.6 g.); (b), b. p. $65 \cdot 5^{-}$, 76° , n_2^{b} 1.4772, n_2^{00} 1.4830 (9.7 g.); (c), b. p. 76° , n_2^{00} 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_2^{01} 1.4758 (Found : C, 74.75; H, 8.5. C₆H₈O requires C, 74.95; H, 8.4%). Similarly redistilled, the pure *trans*-isomer (c) had n_2^{01} 1.4848 (Heilbron, Jones, Smith, and Weedon ³ give b. p. 97—81°/30 mm., $n_2^{18.5}$ 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. C₁₉H₁₆O₂N₂ 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., $n_{\rm p}^{\rm n}$ 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_D⁶⁻⁵ 1·4750—1·4752 (39·8 g.); (b) b. p. 52·7—64·0°, n_D⁶⁻⁵ 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., $n_{\rm D}^{16\cdot5}$ 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. C₆H,Cl requires C, 62.9; H, 6.15; Cl, 30.95%; the trans-isomer (c and d; total yield 110.7 g.) had n_{20}^{20} 1.4850 (Found : C, 63.25; H, 6.1%). Unlike the pent-2-en-4-ynes, the chlorohexenynes 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. $70^{\circ}/82 \text{ mm.}$ — $79^{\circ}/40 \text{ mm.}$, $n_{\rm D}^{17.6}$ 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. $48-50^{\circ}$, $n_{\rm D}^{19}$ 1·4538 (4·7 g.); (b), b. p. 50° , $n_{\rm D}^{19}$ 1·4570 (14·5 g.); (c), b. p. $50-65\cdot5^{\circ}$, $n_{\rm D}^{19}$ 1·4650—1·4832 (9·4 g.); (d), b. p. $65\cdot5^{\circ}$, $n_{\rm D}^{19}$ 1·4870—1·4874 (13·1 g.); (e), b. p. $65\cdot5-75^{\circ}$, $n_{\rm D}^{19}$ 1·4906 (10·3 g.). Distillation of the still residues

¹¹ Mills, J., 1951, 2332.

2599

gave additional material (27 g.) (h), b. p. $65-67^{\circ}/89$ 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. C₅H₅Cl 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-2en-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.), $n_{\rm p}^{19}$ 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 (MgSO₄), 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. C₅H₆O 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. C₁₈H₁₄O₂N₂ 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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