532. *Stereochemical Studies of Olefinic Compounds. Part VI.* Preparation of the Four Stereoisomeric Sorbyl Alcohols from a Single Precursor.*

By L. Crombie, S. H. Harper, and R. J. D. Smith.

The four stereoisomeric hexa-2 : 4-dienols (sorbyl alcohols) are prepared from 4-toluene-*p*-sulphonyloxypent-1-yne. The latter is converted, by an elimination reaction and fractionation, into the known *cis*- and *trans*-pent-3-en-1-ynes. From these, hex-*cis*- and -*trans*-4-en-2-ynols are prepared. Partial catalytic hydrogenation gives hexa-*cis*-2 : *cis*-4- and -*cis*-2 : *trans*-4-dienol respectively, whilst reduction with lithium aluminium hydride gives hexa-*trans*-2 : *cis*-4- and -*trans*-2 : *trans*-4-dienol. The sorbyl alcohols are compared with specimens obtained by independent routes.

In recent work it has been possible to synthesise all four stereochemical forms of unsymmetrical conjugated dienes. The first examples reported[1] were the deca-2 : 4-dienoic acids, their methyl esters and other derivatives, and the deca-2 : 4-dienols. The latter were obtained from the methyl decadienoates by reduction with lithium aluminium hydride: it was shown that this reagent does not cause stereomutation. Soon after, Allan, Jones, and Whiting reported[2] that with their preparation of hexa-*trans*-2 : *cis*-4- and -*cis*-2 : *cis*-4-dienoic acid, the four stereoisomeric sorbic acids were known. The present work concerns the four sorbyl alcohols which were of interest in connexion with the stereoisomeric nona-5 : 7-dien-2-ones. Formally, they should be obtainable from the corresponding sorbic esters by reduction with lithium aluminium hydride, but we have used a single precursor for their preparation. During this work, Butenandt, Hecker, and Zachau[3] reported that they had made these substances by different means and their results are mentioned below. According to Butenandt *et al.*,[3,4] the sorbyl alcohols are of interest in connection with the sex-attractant substance of the silk-spinner.

The primary precursor used in our work was 4-toluene-*p*-sulphonyloxypent-1-yne which was converted into pent-3-en-1-yne by treatment with alkali.[5] Pent-3-en-1-yne obtained by this procedure is a mixture of *cis*- and *trans*-isomers[6] which were separated by distillation. The two hydrocarbons were converted into their Grignard reagents and the latter treated with formaldehyde to give *cis*- and *trans*-hex-4-en-2-ynol. Catalytic partial

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* Part V, *J.*, 1956, 136.

[1] Crombie, *J.*, 1955, 1007.

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

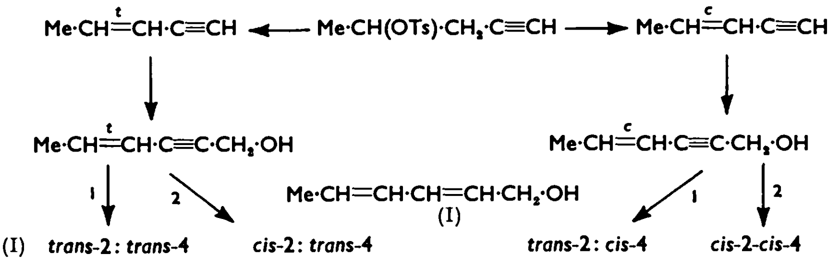
[3] Butenandt, Hecker, and Zachau, *Chem. Ber.*, 1955, **88**, 1185.

[4] Butenandt, *Jahresber. preuss. Akad. Wiss.*, 1939, 97; *Naturwiss. Rdsch.*, 1955, **8**, 457.

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

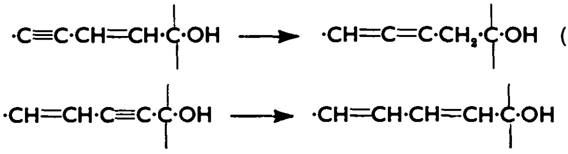
[6] Allan and Whiting, *J.*, 1953, 3314; cf. Bruun, Christensen, Haug, Stene, and Sörensen, *Acta Chem. Scand.*, 1951, **5**, 1244.

hydrogenation of these alcohols, with quinoline-treated Lindlar catalyst [7] and absorption of 0·9 mol. of hydrogen, gave, after distillation, hexa-*cis*-2 : *cis*-4- and -*cis*-2 : *trans*-4-dienol which were characterised as crystalline α-naphthylurethanes. Light absorption data in Tables 1 and 2 relate to materials purified by distillation only, and not regenerated from recrystallised derivatives.



[1, LiAlH$_4$. 2, H$_2$-Lindlar catalyst. Ts = *p*-C$_6$H$_4$Me·SO$_2$]

It has recently been shown [8] that treatment of an enyne system (II) with lithium aluminium hydride gives an allene (III) whereas the related enyne (IV) gives the conjugated diene (V). The behaviour of *cis*- and *trans*-hexenynol is in agreement, the former


(II) (III) (IV) (V)

$$\text{(II)}\ \cdot\text{C}{\equiv}\text{C}\cdot\text{CH}{=}\text{CH}\cdot\overset{|}{\underset{|}{\text{C}}}\cdot\text{OH} \longrightarrow \cdot\text{CH}{=}\text{C}{=}\text{C}\cdot\text{CH}_2\cdot\overset{|}{\underset{|}{\text{C}}}\cdot\text{OH}\ \text{(III)}$$

$$\text{(IV)}\ \cdot\text{CH}{=}\text{CH}\cdot\text{C}{\equiv}\text{C}\cdot\overset{|}{\underset{|}{\text{C}}}\cdot\text{OH} \longrightarrow \cdot\text{CH}{=}\text{CH}\cdot\text{CH}{=}\text{CH}\cdot\overset{|}{\underset{|}{\text{C}}}\cdot\text{OH}\ \text{(V)}$$

giving hexa-*trans*-2 : *cis*-4-dienol and the latter hexa-*trans*-2 : *trans*-4-dienol. For data see Tables.

TABLE 1. *Data for the stereoisomeric hexa-2 : 4-dienols.*

Hexadienol	Source	$\lambda_{max.}$ (mμ)	ε	α-Naphthyl-urethane, m. p.	Hexadienol	Source	$\lambda_{max.}$ (mμ)	ε	α-Naphthyl-urethane, m. p.
trans-2 : *trans*-4	1	227	24,500	98—99°	*cis*-2 : *trans*-4 ...	1	229	19,800	96·5—97·5
	2	227	25,500	99·5—100		4	229	22,100	96—97
trans-2 : *cis*-4 ...	1	230	23,500	100—101	*cis*-2 : *cis*-4	1	230	14,700	88·5—89·5
	3	229·5	21,450	99—101		3	231	16,850	89—90

Sources: 1, From 4-toluene-*p*-sulphonyloxypent-1-yne. 2, From hexa-*trans*-2 : *trans*-4-dienoic ester. 3, Data given by Butenandt *et al.*[3]; see also Experimental section. 4, From hexa-*cis*-2 : *trans*-4-dienoic acid.

TABLE 2. *Comparison of infrared bands of stereoisomeric hexa- and deca-2 : 4-dienols* [1] *(films) and their tentative assignments.*

Dienol	νC=C$_{I}$	νC=C$_{II}$	Mean νC=C	ΔC=C	δ′(CH=CH)$_2$		
Hexa-*trans*-2 : *trans*-4	1661	1626 [a]	1644	35	1003i	987	— [b]
Deca-*trans*-2 : *trans*-4	1660	1626	1643	34	1008i	986	—
Hexa-*trans*-2 : *cis*-4	1653	1613	1633	40	999	982	947
Deca-*trans*-2 : *cis*-4	1655 [c]	1616 [c]	1635	39	1003	983	948
Hexa-*cis*-2 : *trans*-4	1653	1613	1633	40	1001	986	952
Deca-*cis*-2 : *trans*-4	1652	1609	1630	43	997i	984	952
Hexa-*cis*-2 : *cis*-4	1647	1600	1624	47	—	— [d]	— [d]
Deca-*cis*-2 : *cis*-4	1651	1601	1626	50	—	— [d]	— [d]

[a] There is a similar band at 1605 cm.$^{-1}$ which is absent in deca-*trans*-2 : *trans*-4-dienol. [b] There is a band at 950 cm.$^{-1}$ which probably is not of stereochemical significance. [c] Other weak bands occur in this region. [d] Weak bands or inflexions in this region are neglected as they are likely to be due to impurity or other causes and are probably not of stereochemical significance.

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[7] Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

[8] Chanley and Sobotka, *J. Amer. Chem. Soc.*, 1949, **71**, 4140; Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094; Bharucha and Weedon, *J.*, 1953, 1584; Bates, Jones, and Whiting, *J.*, 1954, 1854; Oroshnick, *J. Amer. Chem. Soc.*, 1955, **77**, 4048.

To confirm the identity of the above specimens and estimate their purity, it was necessary to examine sorbyl alcohols from different sources. Hexa-*trans*-2 : *trans*-4-dienol is well known[9] and was prepared by reduction of ethyl *trans-trans*-sorbate with lithium aluminium hydride. Hexa-*cis*-2 : *trans*-4-dienol was made by similar reduction of hexa-*cis*-2 : *trans*-4-dienoic acid which is produced by treating δ-hexenolactone with sodium methoxide in methanol :[10] preparation of this hexadienol by a similar route has since been reported by Butenandt *et al.*[3] The *cis*-2 : *trans*-4 alcohol made by this method is rather purer, as judged by ultraviolet data, than that from the pentenyne route and reflects the inability of currently used catalysts to achieve a high degree of selectivity during the partial hydrogenation of enynes and diynes.

The independent preparation of hexa-*trans*-2 : *cis*-4-dienol was approached through the Reformatski reaction between but-2-ynal and ethyl bromoacetate. For large-scale preparation of 1 : 1-diethoxybut-2-yne a procedure based on Claisen's[11] and Viguier's[12] work was employed (cf. Lunt and Sondheimer[13]) and the acetal was converted into but-2-ynal by the method of Lunt *et al.* Reformatski reaction gave ethyl 3-hydroxyhex-4-ynoate which was dehydrated with phosphoric oxide to ethyl hex-*trans*-2-en-4-ynoate. Semihydrogenation of ethyl 3-hydroxyhex-4-ynoate gave ethyl 3-hydroxyhex-*cis*-4-enoate but, as experienced with an analogue of this acid,[1] no dehydration procedure could be found which did not cause complete or partial stereomutation of the *cis*-4-linkage. Partial hydrogenation of ethyl hex-*trans*-2-en-4-ynoate in the usual way gave ethyl hex-*trans*-2 : *cis*-4-enoate which was reduced to hexa-*trans*-2 : *cis*-4-dienol. The extinction coefficient of the latter (18,400) made it clear that some overhydrogenated material was present but work on the purification of this (and of hexa-*cis*-2 : *cis*-4-dienol which we had made from hexa-2 : 4-diynol and converted into the α-naphthylurethane) was discontinued when Butenandt's paper appeared giving the necessary reference data.

Butenandt *et al.* prepared hexa-*trans*-2 : *cis*-4-dienol by partial hydrogenation of hex-2-en-4-yn-1-ol and hexa-*cis*-2 : *cis*-4-dienol by similar treatment of hexa-2 : 4-diynol. As has been our experience,[1, 14] the hydrogenation was incompletely selective and the alcohols were converted into crystalline 3-nitrophthalates, purified by Craig distribution and then regenerated. The regenerated alcohols were obtained only on a small scale (*e.g.*, 31 mg. of the *cis-cis*-alcohol) but provide a valuable reference for ultraviolet data. Table 1 indicates that, judged by this criterion, our hexa-*trans*-2 : *cis*-4-dienol was a little purer than Butenandt's even though it had only been purified by distillation, but the *cis-cis*-specimen was a little less pure. In each case the α-naphthylurethane of the hexadienol prepared from 4-toluene-*p*-sulphonyloxypent-1-yne did not depress the m. p. of the corresponding compound obtained by an independent route. In agreement with Butenandt *et al.*, we find that admixture of any pair of stereoisomeric α-naphthylurethanes causes a clear melting-point depression.

The data in Table 1 show the characteristic shift of $\lambda_{\text{max.}}$ to longer wavelength on passing through the sequence *trans-trans*, *trans-cis*, and *cis-trans* to *cis-cis*. This is now well established for conjugated dienes,[15] trienes,[15] and tetraenes[16] and contraverts Zechmeister's generalisation[17] based on compounds of the carotenoid type. The decline in $\varepsilon_{\text{max.}}$ is also in agreement with previous data. Although infrared curves were recorded for the 3-nitrophthalates of the hexadienols, Butenandt and his colleagues only report data for the 10 μ region for the alcohols themselves. We find that the bands in the C=C stretching

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[9] Reichstein, Ammann, and Trivelli, *Helv. Chim. Acta*, 1932, **15**, 261; Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 2548.

[10] Eisner, Elvidge, and Linstead, *J.*, 1953, 1372.

[11] Claisen, *Ber.*, 1911, **44**, 1161.

[12] Viguier, *Compt. rend.*, 1909, **149**, 403; *Ann. Chim. (France)*, 1913, **28**, 433.

[13] Lunt and Sondheimer, *J.*, 1950, **3361**.

[14] Crombie, Harper, and Newmann, *J.*, 1956, 3963.

[15] See Crombie and Jacklin, *J.*, 1957, 1632, for references.

[16] Holme, Jones, and Whiting, *Chem. and Ind.*, 1956, 928.

[17] Zechmeister, *Experientia*, 1954, **10**, 1.

region resemble those of the stereoisomeric deca-2 : 4-dienols[1] in that the doublet due to vibrational interaction moves progressively to lower frequencies and the frequency difference increases through the stereochemical sequence given above (Table 2). The *trans*-2 : *trans*-4-alcohol shows the expected strong band at 987 cm.$^{-1}$ but there is also weak absorption at 950 cm.$^{-1}$. As expected,[18] the *trans*-2 : *cis*-4-form has a pair of bands at 982 and 947 cm.$^{-1}$, and the *cis*-2 : *trans*-4-form has them at 986 and 952 cm.$^{-1}$. There is also a maximum or shoulder between 1003 and 999 cm.$^{-1}$ in all three of the above compounds and a somewhat similar situation is found in the decadienols. Beyond small inflexions on the skirt of the band with its maximum at 1015 cm.$^{-1}$, there are no maxima in the spectrum of the *cis-cis*-isomer in this region.

EXPERIMENTAL

Ultraviolet data were determined in EtOH with a Unicam S.P. 500 instrument.

Hex-cis-4-*en*-2-*yn*-1-*ol*.—A Grignard reagent was prepared from magnesium (28 g.) and ethyl bromide (128 g.) in anhydrous ether (250 ml.) and cooled to 0°, and *cis*-pent-3-enyne[5, 6] (76 g.) in anhydrous ether (100 ml.) was added with stirring during 2 hr. The mixture was heated under reflux for 90 min. with stirring, then cooled to 0°, and paraformaldehyde (45 g.; dried over P_2O_5) sublimed into the stirred solution in a current of dry nitrogen. The product was heated under reflux for 1 hr. and set aside for 12 hr. Iced sulphuric acid (700 ml.) was then added with cooling. The ethereal layer was separated and the aqueous layer extracted with ether. The united ethereal solutions were washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated to give *hex*-cis-4-*en*-2-*yn*-1-*ol* (40 g., 36%), b. p. 84—84·5°/18 mm., n_D^{20} 1·5016—1·5020. A second preparation (51% yield) had n_D^{20} 1·5006—1·5009 (Found: C, 74·6; H, 8·6. C_6H_8O requires C, 74·95; H, 8·4%). Light absorption: max. 225 mμ (ε 12,100). The α-*naphthylurethane* crystallised in needles [from light petroleum (b. p. 60—80°)], m. p. 110—111° (Found: C, 76·6; H, 5·7. $C_{17}H_{15}O_2N$ requires C, 76·95; H, 5·7%). On hydrogenation *cis*-hexenynol absorbed 3·0 H_2: the α-naphthylurethane of the product had m. p. 58° undepressed by an authentic sample of *n*-hexyl α-naphthylurethane.

Hex-trans-4-*en*-2-*yn*-1-*ol*.—In one run, use of the procedure described for the *cis*-isomer with *trans*-pent-3-enyne[5, 6] (20 g.), gave *hex*-trans-4-*en*-2-*yn*-1-*ol* (7·5 g., 27%), b. p. 87—89°/23 mm. In a second run on the same scale, the condenser became blocked with paraformaldehyde and the latter may have been added under slight pressure. This gave 48·0 g. of product (72%), b. p. 89—91°/25 mm. The final complex was orange whereas that from *cis*-pentenyne was colourless. The two products were united and redistilled, to give hex-*trans*-4-en-2-yn-1-ol (52 g.), b. p. 90·5—91·5°/22 mm., n_D^{20} 1·5037—1·5039 (Found: C, 74·9; H, 8·6%). Light absorption: max. 225 mμ (ε 12,500). The α-*naphthylurethane* formed clusters of needles, m. p. 114—115°, depressed to 73—76° when admixed with the derivative of the *cis*-isomer (Found: C, 77·4; H, 5·85%). On hydrogenation *trans*-hexenynol absorbed 3·0 H_2, to give *n*-hexanol which was characterised as *n*-hexyl α-naphthylurethane, m. p. and mixed m. p. 58°.

Hexa-trans-2 : trans-4-*dien*-1-*ol*.—Hex-*trans*-4-en-2-yn-1-ol (4·8 g.) in anhydrous ether (10 ml.) was added dropwise and with stirring to powdered lithium aluminium hydride (1·2 g.) suspended in ether (20 ml.). The mixture was stirred and heated under reflux for 3 hr., then cooled in ice and cautiously decomposed with water and then 2N-sulphuric acid (60 ml.). The ethereal layer was separated, washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated. Distillation gave hexa-*trans*-2 : *trans*-4-dien-1-ol (3·5 g., 73%), b. p. 82—83°/18 mm., m. p. 22° without recrystallisation (Found: C, 72·9; H, 10·25. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·3%). Microhydrogenation: 2·0H_2. The α-naphthylurethane crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 98—99°, undepressed by an authentic specimen (below).

Hexa-trans-2 : cis-4-*dien*-1-*ol*.—Hex-*cis*-4-en-2-yn-1-ol (4·8 g.) was reduced with lithium aluminium hydride as described for the *trans*-compound to give hexa-*trans*-2 : *cis*-4-dien-1-ol (4·0 g., 83%), b. p. 83—84°/17 mm., n_D^{20} 1·5000—1·5003 (Found: C, 73·6; H, 10·5%). Microhydrogenation: 2·0 H_2. The α-naphthylurethane had m. p. 100—101° alone or mixed with the specimen described below.

Hexa-cis-2 : trans-4-*dien*-1-*ol*.—Hex-*trans*-4-en-2-yn-1-ol (4·9 g.) was shaken for 1 hr. with

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[18] See refs. 1 and 2 for literature.

Raney nickel (*ca.* 1 g.) in methyl acetate. The nickel was filtered off and washed with methyl acetate, Lindlar's catalyst (1·5 g.) and quinoline (0·2 g.) were added to the filtrate, and the whole was shaken in hydrogen until hydrogen (1150 ml.) had been absorbed (calc. for 1 H_2, 1230 ml.). The catalyst was filtered off, the solvent removed *in vacuo*, and the residue distilled, to give hexa-*cis*-2 : *trans*-4-dien-1-ol (1·35 g., 27%), b. p. 79—80·5°/15 mm., n_D^{20} 1·4942—1·4951 (Found : C, 72·8; H, 10·15%). Microhydrogenation : 2·0 H_2. The α-naphthylurethane had m. p. and mixed m. p. 96·5—97·5°.

Hexa-cis-2 : cis-4-*dien*-1-*ol*.—Hex-*cis*-4-en-2-yn-1-ol (4·9 g.) was pre-treated with Raney nickel (1 g.) in ethyl acetate as above, then filtered, and the nickel washed. Lindlar catalyst (1·0 g.) and quinoline (0·2 g.) were added to the filtrate plus washings, and the mixture hydrogenated until 1130 ml. of gas had been absorbed (calc. for 1 H_2, 1210 ml.). Working up, and two distillations, gave hexa-*cis*-2 : *cis*-4-dien-1-ol (0·6 g., 12%), b. p. 79—81°, n_D^{20} 1·4840—1·4850 (Found : C, 73·7; H, 10·4%). Microhydrogenation : 2·0 H_2. The α-naphthylurethane had m. p. 88·5—89·5°.

Hexa-trans-2 : trans-4-*dien*-1-*ol*.—Reduction of ethyl sorbate (21·5 g.) in ether (50 ml.) by adding the solution to lithium aluminium hydride (3·0 g.) in ether (150 ml.) and working up in the usual way gave hexa-*trans*-2 : *trans*-4-dien-1-ol (12·8 g., 85%), b. p. 81·5—82·5°/14 mm., m. p. 28·5—29°. The α-naphthylurethane had m. p. 99·5—100° (lit.,[3, 9] m. p. 30·5—31·5°; α-naphthylurethane, m. p. 100·5°).

Hexa-cis-2 : trans-4-*dien*-1-*ol*.—Hexa-cis-2 : *trans*-4-dienoic acid was prepared from δ-hexenolactone by the method of Eisner, Elvidge, and Linstead.[10] The lactone (22·4 g.), added to sodium (4·6 g.) in absolute methanol (700 ml.) at 15°, gave, on working up, methyl hexa-*cis*-2 : *trans*-4-dienoate (0·95 g., 5%), b. p. 64—65°/13 mm., n_D^{20} 1·4954—1·4956, and hexa-*cis*-2 : *trans*-4-dienoic acid (16 g., 71%). The latter (m. p. 28°) was not further purified, but added in dry ether (100 ml.) to lithium aluminium hydride (5·45 g.) in ether (200 ml.) at such a rate as to maintain gentle refluxing. After decomposition with water and 3N-sulphuric acid, the product was worked up in the usual way, to give hexa-*cis*-2 : *trans*-4-dienol (7·63 g., 54%), b. p. 70—72°/9 mm., n_D^{20} 1·4955—1·4964 (Found : C, 72·8; H, 10·2%). The 3 : 5-*dinitrobenzoate* crystallised from light petroleum (b. p. 60—80°) in yellow plates, m. p. 86—86·5° (Found : C, 53·2; H, 4·15. $C_{13}H_{12}O_6N_2$ requires C, 53·4; H, 4·15%). The *phenylurethane* crystallised in plates, m. p. 62·5—63·5° (Found : C, 71·8; H, 7·05. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 6·95%). The α-naphthylurethane had m. p. 96—97°. On hydrogenation the diene alcohol absorbed 2·0 H_2, to give *n*-hexanol (α-naphthylurethane, m. p. and mixed m. p. 58°). Butenandt *et al.*[3] give b. p. 50—52°/3—5 mm., and α-naphthylurethane, m. p. 98—99·5°.

1 : 1-*Diethoxybut*-2-*yne*.—Redistilled crotonaldehyde (250 g.) was stirred and cooled in ice, and then bromine (185 ml.) was added during 90 min. Finally crotonaldehyde (3·6 g.) was added to decolorise the product. Anhydrous potassium acetate (425 g.) was added in portions with stirring, at <30°, and the product stirred for 1 hr. Water (100 ml.) was added and the mixture steam-distilled. The heavy layer which separated from the distillate was extracted with ether and the extract washed with portions of sodium carbonate solution. The extract was dried, washed, and distilled, to give α-bromocrotonaldehyde (323 g., 60%), b. p. 57—59°/10 mm. Dry ethanol (380 ml.), ethyl orthoformate (355 g.), and concentrated hydrochloric acid (4 ml.) were added to the aldehyde. Reaction began at once, the temperature rising to 55°. As soon as the temperature began to fall, the excess of ethyl orthoformate and the ethanol were distilled off through a short Vigreux column. Anhydrous sodium carbonate (6 g.) was added to the residue, which was filtered and distilled, to give α-bromocrotonaldehyde diethyl acetal (394 g., 82%), b. p. 82—84°/10 mm., n_D^{20} 1·4580 (Viguier[12] gives b. p. 86°/15 mm., n_D^{21} 1·4565).

The acetal (394 g.) was heated under reflux for 2½ hr. with potassium hydroxide (140 g.) in methanol (1·5 l.). The methanol was distilled off through a short column and water added to the residue. The organic layer was separated with the aid of ether, dried, evaporated, and distilled, to give 1 : 1-diethoxybut-2-yne (217 g.), b. p. 65—67°/12 mm., n_D^{20} 1·4296. A further 12 g. of this product were obtained by subjecting the distillation residue to further alkaline hydrolysis. The overall yield was 44% : runs on a 7-molar scale gave 40—42% yields. The method is well suited for large-scale work.

1 : 1-Diethoxybut-2-yne (48% yield in two experiments) was also prepared by Lunt and Sondheimer's method[13] and had b. p. 56—59°/9 mm., n_D^{20} 1·4285. The latter authors give b. p. 62—63·5°/14 mm., n_D^{20} 1·4290, and claim a yield of 80%.

But-2-yn-1-al.—1 : 1-Diethoxybut-2-yne (40 g.) was shaken for 12 hr. under nitrogen with saturated aqueous tartaric acid (40 ml.) and quinol (0·15 g.). Saturated calcium chloride solution (180 ml.) was added and after 3 minutes' shaking the product was extracted four times with ether. Drying, evaporation (short column), and distillation gave but-2-yn-1-al (4·9 g., 26%), b. p. 105—108°, n_D^{20} 1·4468. Acetal (15·0 g., 37·5%) was recovered. In our hands, yields of aldehyde have varied between 26 and 30%. Lunt and Sondheimer [13] give b. p. 105—110°, n_D^{20} 1·4456, average yield 35%.

*Ethyl 3-Hydroxyhex-*cis*-4-enoate.*—Zinc wool (5 g.) was activated by brief immersion in 2N-hydrochloric acid, washed with water, alcohol, acetone, and ether, and dried at 100°. The zinc was covered with dry benzene (10 ml.) and heated under reflux. A mixture of but-2-ynal (4·9 g.), ethyl bromoacetate (12·0 g.), and benzene (10 ml.) was added in portions (reaction began about 5 min. after the first addition). Then the mixture was stirred and heated under reflux for 1 hr., cooled in ice, and stirred for 1 hr. with 10% acetic acid (60 ml.). The benzene layer was separated, dried ($MgSO_4$), evaporated, and distilled, to give ethyl 3-hydroxyhex-4-ynoate (3·06 g., 27%), b. p. 70—71°/0·1 mm., n_D^{20} 1·4572.

The ester (2·34 g.) was hydrogenated at 5% palladium–barium sulphate (0·25 g.) in methyl acetate (5 ml.) until 1 mol. of hydrogen had been absorbed. Filtration, evaporation, and distillation gave *ethyl 3-hydroxyhex-*cis*-4-enoate,* (1·99 g., 84%), b. p. 59—59·5°/0·06 mm., n_D^{20} 1·4469 (Found : C, 60·5; H, 9·4. $C_8H_{14}O_3$ requires C, 60·7; H, 8·9%.)

*Dehydration of Ethyl 3-Hydroxyhex-*cis*-4-enoate.*—(i) The hydroxy-ester (0·9 g.) was heated to 170° for 1 hr. in nitrogen with powdered potassium hydrogen sulphate (0·76 g.). The product was cooled, water (5 ml.) added, and the organic layer removed by extraction with ether. The extract was dried, evaporated, and distilled (0·1 g.; b. p. 84—86°/12 mm., n_D^{20} 1·4950). Its infrared spectrum showed that it was mainly ethyl hexa-*trans*-2 : *trans*-4-dienoate.

(ii) The hydroxy-ester (0·4 g.) was heated under reflux for 1 hr. with benzene (1 ml.), pyridine (1 ml.), and phosphorus oxychloride (0·7 g.). The product was diluted with benzene (2 ml.) and washed successively with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, then dried ($MgSO_4$), and the benzene evaporated. Distillation gave an ester (0·12 g.), b. p. 83—84°/14 mm., n_D^{20} 1·4926. Light absorption : max. 258 mμ (ε 29,200). The infrared spectrum showed it to be almost pure ethyl hexa-*trans*-2 : *trans*-4-dienoate.

(iii) The hydroxy-ester (4·2 g.) was mixed with phosphoric oxide (4·5 g.); reaction set in and the mixture became brown. Removal of the product *in vacuo* and redistillation gave an ester, b. p. 77—78°/9 mm., n_D^{20} 1·4870—1·4900. Light absorption : max. 258 mμ (ε 23,700). The infrared absorption showed it to contain large amounts of ethyl hexa-*trans*-2 : *trans*-4-dienoate.

*Ethyl Hex-*trans*-2-en-4-ynoate.*—Ethyl 3-hydroxyhex-4-ynoate (6·7 g.) was mixed with phosphoric oxide (5 g.); heat was produced and the mixture became brown. Distillation gave a product, b. p. 78—82°/9 mm., n_D^{20} 1·4940, which when redistilled gave ethyl *hex-*trans*-2-en-4-ynoate* (2·34 g., 39%), b. p. 79·5—81°/9 mm., n_D^{20} 1·4958—1·4962 (Found : C, 68·7; H, 7·0. $C_8H_{10}O_2$ requires C, 69·5; H, 7·3%). Microhydrogenation : 3·0 H_2. Light absorption : max. 257 mμ (ε 19,000). For preparative work, phosphoric oxide was heated to 130° *in vacuo* and an equal weight of ethyl 3-hydroxyhex-4-ynoate added dropwise; the enyne ester distilled continuously. Redistillation of the crude product gave enyne ester (30—48%), b. p. 90—92°/12 mm., n_D^{20} 1·4963.

*Hexa-*trans*-2 :* cis*-4-dien-1-ol.*—Ethyl hex-*trans*-2-en-4-ynoate (23·4 g.) was hydrogenated in ethyl acetate (75 ml.) over Lindlar catalyst (7·0 g.) in the presence of quinoline (1·2 g.). Reduction was interrupted when hydrogen (3·72 l. at 17°/750 mm.) had been absorbed (calc. for absorption of 1 mol., 3·9 l.). Two careful fractionations gave ethyl hexa-*trans*-2 : *cis*-4-dienoate (13·4 g., 54%), b. p. 85·5—86·5°/18 mm., n_D^{20} 1·4858—1·4872. Light absorption : max. 261 mμ (ε 21,000). Microhydrogenation : 2·0 H_2. Allan *et al.*[2] give max. 262 mμ (ε 23,500) for the methyl ester.

The ethyl ester (13·2 g.) in anhydrous ether (50 ml.) was added during 90 min. to lithium aluminium hydride (3·35 g.) in ether (70 ml.) under nitrogen. After stirring (15 min.), ice-water was added cautiously and then 2N-sulphuric acid. Isolation in the usual way gave hexa-*trans*-2 : *cis*-4-dien-1-ol (7·32 g., 78%), b. p. 79—81°/15 mm., n_D^{20} 1·4982 (there was considerable frothing during the distillation) (Found : C, 73·0; H, 10·5%). Light absorption : max. 229 mμ (ε 18,400). The 3 : 5-*dinitrobenzoate* formed pale yellow leaflets, m. p. 73° (Found : C, 53·2; H, 4·3. $C_{13}H_{12}O_6N_2$ requires C, 53·4; H, 4·15%). The α-naphthylurethane had m. p. 99—100° (Found : C, 76·1; H, 6·7. Calc. for $C_{17}H_{17}O_2N$: C, 76·4; H, 6·4%). On microhydrogenation

$2{\cdot}0\ H_2$ were absorbed and the product was identified as *n*-hexanol (α-naphthylurethane, m. p. and mixed m. p. 59°).

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(L. C.) ORGANIC CHEMISTRY DEPARTMENT, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, LONDON, S.W.7.
(S. H. H. AND R. J. D. S.) KING'S COLLEGE,
STRAND, LONDON, W.C.2.

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