sulfoxide–heavy water mixture with tetramethylsilane as internal standard. When measurements were performed on the compound in the DMSO–protium oxide system, differences were found in the coupling of H^c and in addition the integral of the H^c signal was twice that in the DMSO–deuterium oxide mixture. Thus it is evident that the studied reaction proceeds by route (2), for another product would be obtained if proton transfer to the 4-position were rate determining.

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1. Stamhuis, E. J., Drenth, W. and van der Berg, H. *Rec. Trav. Chim.* **83** (1964) 167.
2. Kankaanperä, A. and Kleemola, S. *Acta Chem. Scand.* **23** (1969) 3607.
3. Salomaa, P., Kankaanperä, A., Nikander, E., Kaipainen, K. and Aaltonen, R. *Acta Chem. Scand. In press.*
4. Unverferth, A. and Schwetlick, K. *J. prakt. Chem.* **312** (1970) 882.
5. Kankaanperä, A. and Salomaa, P. *Acta Chem. Scand.* **21** (1967) 575.
6. Salomaa, P., Kankaanperä, A. and Lajunen, M. *Acta Chem. Scand.* **20** (1966) 1790.
7. Kresge, A. J. and Chiang, Y. *J. Chem. Soc.* **B 1967** 53, 58.

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Formation of Conjugated Dienes on Lithium Aluminium Hydride Reduction of Allenic *tert.*-Alcohols*

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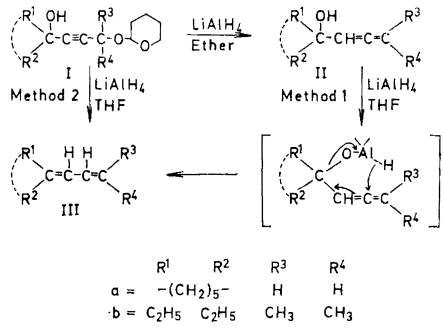
In connexion with the synthesis of allenic *tert.* alcohols for pharmacological evaluation,[1] we noted that the reaction [2] of 1-[3-(tetrahydro-2-pyranyloxy)-1-propynyl]cyclohexanol (Ia) with $LiAlH_4$ to 1-propadienylcyclohexanol (IIa) upon prolonged reaction time afforded a by-product. This compound was identified as the conjugated diene IIIa (*cf.* Scheme 1). Treatment of the allenic alcohol IIa with $LiAlH_4$ in THF gave IIIa in 80 % yield. Under similar conditions as in the latter experiment, the analogous allenic derivative IIb was also found to afford the corresponding diene IIIb.

The reactions were followed by GLC and GLC–MS in order to characterize all products formed. Only in the reaction of IIa to IIIa a by-product of appreciable amount (10 %) was observed. This product was isolated by preparative GLC and, by spectroscopic methods (IR, NMR and MS), identified as 2-propynylidenecyclohexane.

In order to get insight into the mechanism of the reaction II→III we reacted IIa with $LiAlD_4$ in THF. This reaction yielded 2-propenylidenecyclohexane-2-*d* (IIIa-2-*d*), which indicates that the elimination of the hydroxyl group of the allenic alcohol IIa proceeds as outlined in Scheme 1. An analogous mechanism has been proposed [3] for the $LiAlH_4$ reduction of tetraphenylbutyne-1,4-diol to 1,1,4,4-tetraphenylbutadiene-(1,3) [3,4] and for the addition of Grignard reagent to 2,3-butadienol.[5]



Scheme 1.

To check the possibility of preparing the dienes in a one step reaction from the corresponding tetrahydro-2-pyranyloxy derivatives we carried out the reduction of Ia and Ib in THF and obtained 70 % yields of IIIa and IIIb, respectively. This shows that the dienes can be prepared

* Allenes and acetylenes I.

directly from I without isolation of the intermediary allenic alcohols.

Our results indicate that the reaction of allenic *tert.* alcohols with $LiAlH_4$ in THF may be a general method for the synthesis of conjugated dienes.

Experimental. General. IR-spectra were run on a Perkin-Elmer Infracord 337 spectrophotometer using liquid films on NaCl discs. NMR spectra were obtained in $CDCl_3$, if not otherwise stated, using a Varian A 60 spectrophotometer and with tetramethylsilane as internal standard. Mass spectra were run on an AEI MS-30 mass spectrometer connected to a Pye 104 gas chromatograph. The ionizing energy was maintained at 70 eV, the accelerating energy at 4 kV, and the temperature of the source at 200°C.

GLC analyses were run on a Perkin-Elmer F 11 or a Varian 1700 equipped with flame ionization detectors. Columns: 1.5 or 2.3 m glass columns packed with 3 % OV-17 + 1 % succinamide polymer on Gaschrom Q or 5 % Carbovax 20 M on Chromosorb W (60–80 mesh). The preparative column was of aluminium, $\varnothing = 3/8''$, 3 m long and packed with 20 % Carbovax 20 M on Chromosorb W (60–80 mesh). Tetrahydrofuran (THF) was dried over KOH and distilled from $LiAlH_4$.

Elemental analyses were performed in the laboratories of Dr. A. Bernhardt, Mülheim, West Germany.

1-[3-(Tetrahydro-2-pyranyloxy)-1-propynyl] cyclohexanol (Ia). To the Grignard reagent prepared in ether from magnesium (19.5 g; 0.8 mol) and ethyl bromide (87.3 g; 0.8 mol) was added 200 ml of THF. A solution of 3-(tetrahydro-2-pyranyloxy)propyne (98.1 g; 0.7 mol) in 200 ml of THF was then added dropwise to the stirred solution at 15–20°C during 0.5 h. The solution was stirred for another 15 min at room temperature and 63.8 g (0.65 mol) of cyclohexanone in 50 ml of THF added during 1 h. Stirring was continued for 3 h at room temperature and the solution poured on a mixture of ice and 50 % H_2SO_4 (0.3 mol). The alcohol was taken up in light petroleum, washed several times with 25 % $(NH_4)_2SO_4$, twice with water, dried over Na_2SO_4–K_2CO_3 and distilled. B.p. 124–127°/0.3 mmHg. Yield 70 %. (Found: C 70.5; H 9.1. Calc. for $C_{14}H_{22}O_3$: C 70.5; H 9.3.)

3-Ethyl-6-methyl-6-(tetrahydro-2-pyranyloxy)-4-heptyn-3-ol (Ib) was prepared as described for Ia from 42 g (0.25 mol) of 3-(tetrahydro-2-pyranyloxy)butyne,[6] Grignard reagent (0.28 mol), and 19.8 g (0.23 mol) of 3-pentanone. B.p. 96°/0.03 mmHg. Yield: 58 %. (Found: C 71.1; H 10.2. Calc. for $C_{15}H_{26}O_3$: C 70.8; H 10.3.)

1-Propadienylcyclohexanol (IIa). A suspension of 2.5 g of $LiAlH_4$ (0.065 mol) in 200 ml of ether was refluxed with stirring for 20 min whereupon 11 g (0.046 mol) of Ia in 50 ml of ether was slowly added to the ether suspension during continued stirring at such a rate that gentle refluxed was maintained. When the addition was completed, the reaction mixture was refluxed for another 25 min. After cooling, the reaction mixture was cautiously poured into a mixture of ice and 15 ml (0.03 mol) of 2 M H_2SO_4 and worked up as described for Ia. B.p. 92–94°/16 mmHg. Yield: 72 %. The product crystallized in the refrigerator and remained semi-solid at room temperature. IR: 1960 cm^{-1} (s, C=C=C). NMR: δ (ppm) = 5.15 (t, 1H, =CH–), 4.65 (d, 2H, H_2C=, J = 6.5 Hz), 3.7 (s, 1H, –OH), 1.7–1.2 (m, 10H, C_6H_{10}). (Found: C 78.2; H 10.1. Calc for $C_9H_{14}O$: C 78.2; H 10.2.)

2-Propenylidenecyclohexane[7] *(IIIa). Method 1.* To a stirred suspension of 1.9 g (0.05 mol) of $LiAlH_4$ in 100 ml of THF under nitrogen was slowly added 5 g (0.036 mol) of IIa (99 % pure on GLC) dissolved in 25 ml of THF. The mixture was refluxed until the reaction was complete (2.5 h) and worked up as described for IIa. B.p. 63°/45 mmHg. Yield: 75 %.

Pure IIIa was obtained by preparative GLC. IR: 1630 cm^{-1} (m, C=C), 980 cm^{-1} (s, –CH=CH_2) 890 cm^{-1} (s, H_2C=). NMR: δ (ppm) = 6.7–6.1 (m, 1H, H_2C=C*H*–CH=), 5.55 [d, 1H, =CH–C*H*=C(CH_2–)$_2$] 5.0–4.6 (m, 2H H_2C=), 2.3–1.9 [m, 4H, =C(CH_2–)$_2$], 1.6–1.3 [m, 6H, (–CH_2)$_3$–]. Mol. wt. 122 (MS).

The mixture contained 10 % of 2-propynylidenecyclohexane[8] which was isolated by preparative GLC. IR: 3310 cm^{-1} (s, ≡CH), 1620 cm^{-1} (s, C=C). NMR: δ = 5.1–5.0 (m, ≡C–CH=), 2.85 (d, 1H, HC≡, J = 2 Hz), 2.5–2.0 [two m centered at 2.35 and 2.1, 4H, =C(CH_2–)$_2$], 1.6–1.3 [m, 6 H, (–CH_2–)$_3$]. Mol.wt. 120 (MS)

Method 2. To a stirred suspension of 2.28 g (0.06 mol) of $LiAlH_4$ in 100 ml of THF under nitrogen was added a solution of 4.8 g (0.02 mol) of Ia in 20 ml of THF during 15 min. The mixture was refluxed until no allenic alcohol was detectable on GLC (3 h). Work up was performed as for IIa yielding 1.7 g (70 %) of 80 % pure product upon distillation. The impurities were the same as those described under Method 1.

*2-Propenylidenecyclohexane-2-*d *(IIIa-2-*d). IIa (0.9 g, 6.5 mmol) was treated with $LiAlD_4$ (0.4 g; 9.5 mmol) as described for IIIa. Yield: 80 %. NMR: δ (ppm) = 5.7–5.5 (m, 1H, H_2C=CD–C*H*=), 5.0–4.7 (m, 2H, H_2C=),

2.4–1.9 [m, 4H, $=C(CH_2-)_2$], 1.6–1.3. [m, 6H, $(-CH_2)_3-$]. Mol.wt. 123 (MS).

3-Ethyl-6-methyl-4,5-heptadien-3-ol (IIb). Prepared as described for IIa from Ib (10.0 g; 0.039 mol) and $LiAlH_4$ (2.1 g; 0.055 mol) but refluxed for 15 min only. B.p. 70°/10 mmHg. Yield: 78 %. IR: 1960 cm^{-1} (m, C=C=C). Mol.wt. 154 (MS).

5-Ethyl-2-methyl-2,4-heptadiene (IIIb). *Method 1.* Prepared as described for IIIa from IIb (5.0 g; 0.033 mol) and $LiAlH_4$ (1.7 g; 0.045 mol). B.p. 70°/35 mmHg. Yield 90 %. IR: 1610 cm^{-1} (m, C=C), 845 cm^{-1} (s, –CH=) NMR (neat): δ (ppm) = 5.7 (m, 2H, $=CH-CH=$), 2.3–1.8 [two superimposed q, 4H, $=C(CH_2-)_2$], 1.70 and 1.63 [two s, 6H, $=C(CH_3)_2$], 1.0 (t, 6H, $-CH_2-CH_3$), Mol.wt. 138 (MS).

Method 2. The procedure was analogous to that described for IIIa, *Method 2*, starting with Ib. (7.2 g; 0.028 mol) and $LiAlH_4$ (2.7 g; 0.074 mol). Yield: 70 %.

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1. Claesson, A., Bogentoft, C. and Danielsson, B. *To be published.*
2. Cowie, J. S., Landor, P. D. and Landor, S. R. *Chem. Commun.* **1969** 541.
3. Lutz, R. E., Bass, R. G. and Boykin, Jr., D. W. *J. Org. Chem.* **29** (1964) 3660.
4. Kuhn, R. and Schulz, B. *Chem. Ber.* **98** (1965) 3218.
5. Richey, Jr., H. G. and Szucs, S. S. *Tetrahedron Letters* **1971** 3785.
6. Robertson, D. N. *J. Org. Chem.* **25** (1960) 931.
7. Corey, E. J. and Cane, D. E. *J. Org. Chem.* **34** (1969) 3053.
8. Montijn, P. P., Schmidt, H. M., van Boom, J. H., Bos, H. J. T., Brandsma, L. and Arens, J. F. *Rec. Trav. Chim.* **84** (1965) 271.

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The Hydrolysis of α-Sulphanuric Chloride, α-$(NSOCl)_3$

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According to Becke-Goehring[1] the hydrolysis of sulphanuric chloride (I) should lead to sulphanuric acid (II), but that this substance (II) is clearly very unstable and that even on careful acid hydrolysis imidosulphamide (IV) and sulphuric acid are formed immediately, the step from sulphanuric acid (II) to imidosulphamide (IV) presumably being *via* trisulphimide (III).

Hydrolysis of α-sulphanuric chloride with dilute silver nitrate solution yielded silver chloride and also colourless needle-shaped crystals which were identified by X-ray diffraction as the silver salt, $Ag_3(NSO_2)_3 \cdot 5H_2O$, of trisulphimide (III). This shows that in the case of α-$(NSOCl)_3$ hydrolysis is possible with out breaking the ring and supports the view that trisulphimide is an intermediate in the hydrolysis of α-$(NSOCl)_3$.

A crystal structure determination[2] shows that the $(NS)_3$ ring in the trisulphimide ion retains the chair form which exists[3] in α-sulphanuric chloride.

Experimental. The hydrolysis was carried out on a microscope slide using "bench" silver nitrate solution. The sulphanuric chloride was kindly provided by Dr. A. J. Banister.

X-Ray rotation and Weissenberg photographs were taken with Cu$K\alpha$ radiation. Comparison of cell dimensions and intensities with those published by Fischer and Andress[4] established the identity of the hydrolysis product as $Ag_3(NSO_2)_3.3H_2O$.

1. Becke-Goehring, M. *Advan. Inorg. Chem. Radiochem.* **2** (1960) 185.
2. Hazell, A. C., Hazell, R. G. and Ponce, G. A. *Submitted to Acta Cryst.*
3. Hazell, A. C., Wiegers, G. A. and Vos, A. *Acta Cryst.* **20** (1966) 186.
4. Fischer, K. and Andress, K. R. *Z. anorg. Chem.* **281** (1955) 169.

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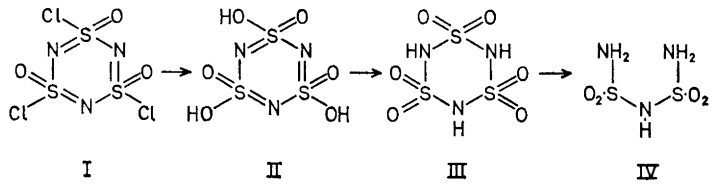

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