Studies on the Stereochemical Course of Selenium-assisted Cyclisation: Biogenetic-type Synthesis in the *p*-Menthan Series

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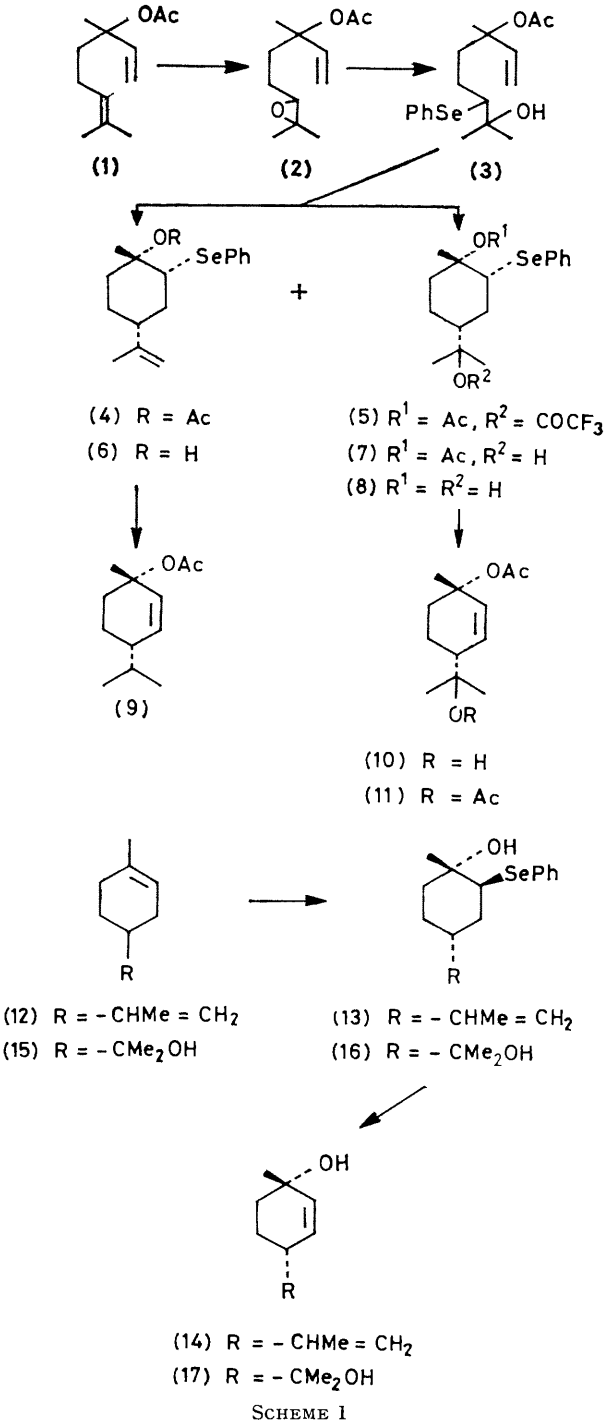
Summary Acid-catalysed cyclisation of the β-hydroxy selenide (**3**) derived from linalyl acetate (**1**) afforded the *trans*-*p*-methans (**4**) and (**5**), the structures of which were confirmed by their transformation into (**6**), (**8**), (**9**), and (**11**) and by alternative synthesis of these compounds

IN the field of polyolefin cyclisation a variety of reagents have been used recently [1,2] As a continuation of our study of the use of organoselenium compounds in the synthesis of natural products[3,4] we investigated the stereochemical course of a selenium-assisted cyclisation reaction resulting in carbon–carbon bond formation and here report a novel intramolecular rearrangement of the phenylselenyl-group during stereoselective olefinic cyclisation

The β-hydroxy selenide (**3**), prepared by the epoxidation of linalyl acetate (**1**) using *m*-chloroperbenzoic acid followed by treatment of the resulting epoxide (**2**) with benzeneselenolate anion,[5] was treated with trifluoroacetic acid in dichloromethane to give the *p*-menthans (**4**) (yield 6 3%) [ν_{max} ($CHCl_3$) 1720 cm^{-1}, δ (CCl_4) 1 70 (3H, s, Me), 1 73 (3H, s, Me), 2 0 (3H, s, OAc), and 4 73 (2 H, br s, olefinic H), *m/e* 350, 352 (M^+)] and (**5**) (yield 36%) [ν_{max} ($CHCl_3$) 1780 and 1730 cm^{-1}, δ (CCl_4) 1 52 (6H, s, 2 Me), 1 75 (3H, s, Me), and 2 0 (3H, s, OAc), *m/e* 464, 466 (M^+)] The structures of compounds (**4**) and (**5**) were established as follows The *p*-menthan (**13**),† obtained from limonene (**12**) by successive treatment with *m*-chloroperbenzoic acid and benzeneselenolate anion, was treated with 30% H_2O_2 followed by heating to give *trans*-*p*-mentha-2,8-dien-1-ol (**14**) ‡ The acetate (**9**), obtained from (**4**) by successive oxidation (30% H_2O_2) and elimination (reflux in benzene) of the phenylselenyl-group, was identical to the compound resulting from acetylation (Ac_2O, dimethylaminopyridine, pyridine) of (**14**), but the alcohol (**6**), prepared by hydrolysis (KOH, EtOH) of (**4**), was not identical to (**13**) These results strongly suggest that the structure of (**4**) is as shown in Scheme 1 Furthermore, the *p*-menthan (**16**), obtained from the α-terpineol (**15**) by successive oxidation (*m*-chloroperbenzoic acid) and epoxide opening with benzeneselenolate anion, was converted into *trans*-*p*-menth-2-en-1,8-diol (**17**) [ν_{max} ($CHCl_3$) 3600 cm^{-1}, δ (CCl_4) 1 17 (3H, s, Me), 1 22 (6H, s, 2 Me), and 5 82 (2H, br s, olefinic H), *m/e* 170 (M^+)] by treatment with 30% H_2O_2 followed by heating The diacetate (**11**), prepared from (**5**) *via* (**7**) by successive hydrolysis (K_2CO_3, MeOH), oxidation (30% H_2O_2), elimination (reflux in benzene), and acetylation (Ac_2O, dimethylaminopyridine, pyridine), was identical to the compound obtained by acetylation of (**17**), but the diol (**8**), resulting from the hydrolysis (KOH, EtOH) of (**7**), was not identical to (**16**) These results suggest that the structure of (**5**) is as shown in Scheme 1



SCHEME 1

† This compound was purified by column chromatography on silica gel using hexane–ethyl acetate (2 1) as eluant and the structure established from comparison of spectroscopic data with those of stereo- and regio-isomers Details will be reported elsewhere

‡ The compound (**14**) thus obtained was identical to an authentic sample by spectral comparison (T Sato and E Murayama, *Bull Chem. Soc Jpn*, **1974**, **47**, 715)

Thus we have shown the stereochemical course of a new type of cyclisation assisted by an organoselenium group and this result may be explained by the reaction mechanism shown in Scheme 2 in which the selenium cation (**20**), generated by participation of olefin in the seleniranium ion (**18**) *via* (**19**), is substituted with a trifluoroacetoxy-group (path a) to give compound (**5**) and deprotonated by a trifluoroacetoxy-group (path b) to afford compound (**4**).

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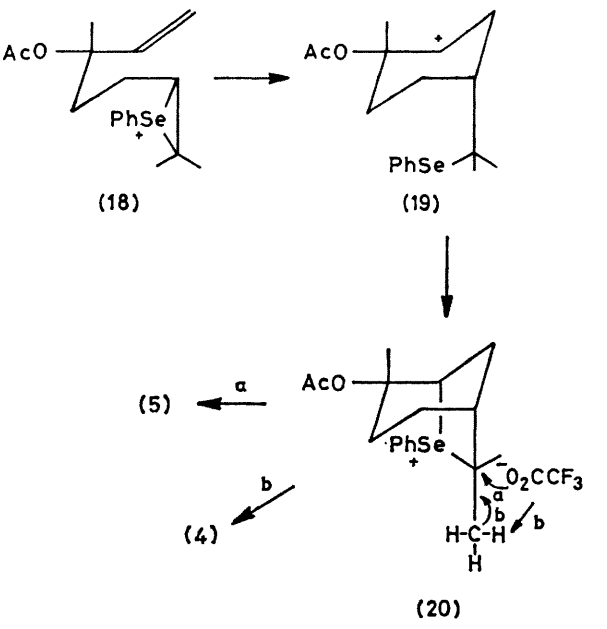

SCHEME 2.

[1] For reviews see M. Julia, *Acc. Chem. Res.*, 1971, **4**, 386; E. E. Van Tamelen, *Acc. Chem. Res.*, 1975, **8**, 152; W. S. Johnson, *Bioorg. Chem.*, 1976, **5**, 51; *Angew. Chem., Int. Edn. Engl.*, 1976, **15**, 9; J. K. Sutherland in 'Stereoselective Synthesis of Natural Products,' Proceedings of the Seventh Workshop Conference, Hoechst, Schloss Reisensburg, 24—27 September, 1978, Eds. W. Bartmann and E. Winterfeldt, Excerpta Medica, Amsterdam–Oxford, 1979, pp. 142—150.

[2] I. Ichinose and T. Kato, *Tetrahedron Lett.*, 1979, 61; Y. Yamada, H. Sanjoh, and K. Iguchi, *ibid.*, p. 1323; M. Matsuki, M. Kodama, and S. Ito, *ibid.*, p. 2901; R. S. Brinkmeyer, *ibid.*, p. 207, F. Bellesia, R. Grandi, U. M. Pagnoni, and R. Trave, *J. Chem. Soc., Perkin Trans. 1*, 1979, 851; W. Renold, G. Ohloff, and T. Norin, *Helv. Chim. Acta*, 1979, **62**, 985; K. E. Harding, *J. Org. Chem.*, 1979, **44**, 2834; M. B. Gravestock, D. R. Morton, S. G. Boots, and W. S. Johnson, *J. Am. Chem. Soc.*, 1980, **102**, 800; E. E. Van Tamelen and D. G. Loughhead, *ibid.*, p. 869.

[3] T. Kametani, H. Nemoto, and K. Fukumoto, *Heterocycles*, 1977, **6**, 1365; *Bioorg. Chem.*, 1978, **7**, 215.

[4] T. Kametani, K. Suzuki, H. Kurobe, and H. Nemoto, *J. Chem. Soc., Chem. Commun.*, 1979, 1128.

[5] K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, 1973, **95**, 2697.