

Halogenated Terpenoids. XVIII*

exo-3-Chlorocamphane (Camphene Hydrochloride)

Raymond M. Carman and Ian M. Shaw

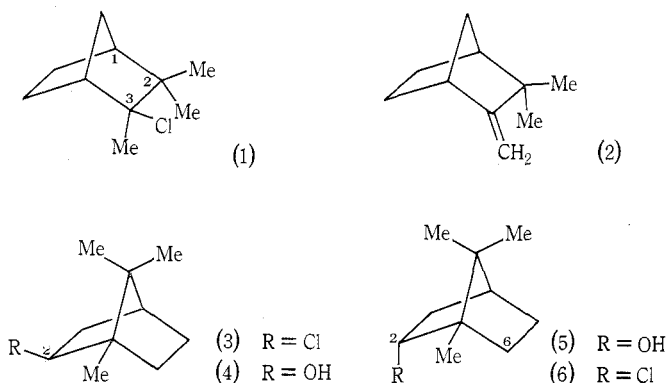
Chemistry Department, University of Queensland,
St. Lucia, Qld. 4067.

Abstract

Camphene hydrochloride is available from the reaction of isoborneol with phosphorus pentachloride.

Discussion

Camphene hydrochloride (1) has played an important historical role in the chemistry of the terpenes and of carbonium ion rearrangements.¹⁻⁶ The compound (1), invariably made by addition of hydrogen chloride to camphene (2), is highly reactive and in the presence of hydrogen chloride rapidly rearranges to *exo*-2-chlorobornane (isobornyl chloride) (3). Recently Brown and Liu⁷ have reviewed the nature of the cation involved in this rearrangement, and report that a 'Brown' automatic hydrochlorinator proved useful in synthesizing chloride (1) from olefin (2).



* Part XVII, *Aust. J. Chem.*, 1979, 32, 2331.

¹ Simonsen, J., and Owen, L. N., 'The Terpenes' 2nd Edn, Vol. 2, p. 307 (Cambridge University Press, 1957).

² Berson, J. A., in 'Molecular Rearrangements' (Ed. P. de Mayo) Vol. 1, p. 113 (Interscience: New York 1963).

³ Bartlett, P. D., 'Non-Classical Ions' p. 48 (W. A. Benjamin: New York 1965).

⁴ Bartlett, P. D., in 'Organic Chemistry. An Advanced Treatise' (Ed. H. Gilman) Vol. 3, p. 65 (John Wiley: New York 1953).

⁵ Eastman, R. H., and Noller, C. R., in 'Organic Chemistry. An Advanced Treatise' (Ed. H. Gilman) Vol. 4, p. 652 (John Wiley: New York 1953).

⁶ Ingold, C. K., 'Structure and Mechanism in Organic Chemistry' 2nd Edn, p. 769 (Cornell University Press: Ithaca, N.Y., 1969).

⁷ Brown, H. C., and Liu, K. T., *J. Am. Chem. Soc.*, 1975, 97, 600.

We now report a further convenient synthesis of chloride (1), with the advantage that excess hydrogen chloride is not present in the reaction. During explorations around the reaction of tertiary alcohols with phosphorus pentachloride,⁸ we observed that isoborneol (4) with phosphorus pentachloride and calcium carbonate in chloroform gave complete conversion into the rearranged tertiary halide (1) within 3 min at 0°. The product (1) was recognized by comparison with authentic material and through the identity of its ¹H n.m.r. spectrum with that recorded by Brown.⁷ The reaction is noteworthy when followed by n.m.r. spectroscopy; we observed the loss of the downfield proton geminal to the secondary hydroxyl (or chlorine) and the clean formation of three new sharp methyl singlets with the methyl geminal to the tertiary chlorine at the characteristic downfield position (δ 1.59). The compound (1) was further identified by its facile rearrangement to isobornyl chloride (3). This rearrangement, in chloroform at room temperature with no added hydrogen chloride, had a half-life of about 7 h. Brown⁷ reports that his sample of chloride (1), which presumably was not free of excess hydrogen chloride, rearranged to (3) within 10 min in ether, more slowly in methylene chloride. Attempts to purify chloride (1) by recrystallization from cold pentane led only to increasing amounts of chloride (3).

The conversion (4) $\rightarrow$ (1) $\rightarrow$ (3) provides an interesting example of two consecutive Wagner–Meerwein rearrangements, readily followed in a n.m.r. spectrometer, in which the final carbon skeleton is identical with that of the initial material.

Borneol (5) with phosphorus pentachloride under the same conditions also gave camphene hydrochloride (1), but the reaction was not as clean and after 3 min at 0° the mixture showed chloride (1) 90%, isobornyl chloride (3) 5% and unchanged borneol (5) 5%. This reaction is slower, presumably because a linear transition state involving C6, C2 and the leaving group cannot develop due to the *endo* orientation at C2.

The reaction between borneol (5) and phosphorus pentachloride has already been reported,^{9–11} but the literature is confused because early workers failed to appreciate the rapid rearrangement of chloride (1) to (3) followed by the much slower conversion into bornyl chloride (6). Kachler⁹ isolated only isobornyl chloride after 2 days in an unbuffered medium. Reychler¹⁰ reported only bornyl chloride, while Wagner and Brickner¹¹ isolated both isobornyl chloride (3) (major) and bornyl chloride (6) (minor). Interestingly, the apparent inversion of C2 configuration in the reaction (5) $\rightarrow$ (3) has been quoted¹² to support the proposition that the reaction of phosphorus pentachloride with secondary alcohols proceeds with inversion of configuration and to provide chemical evidence for the C2 stereochemistry of isobornyl chloride.

Experimental

exo-3-Chlorocamphane (1)

Phosphorus pentachloride (0.14 g) and calcium carbonate (powdered, 0.1 g) were stirred in chloroform (ethanol free, 10 ml) at 0° for 3 min. Isoborneol (4) (0.1 g) was added. The mixture was stirred for a further 3 min and then filtered (sinter). The solution was evaporated to low volume

⁸ Carman, R. M., and Shaw, I. M., *Aust. J. Chem.*, 1976, **29**, 133.

⁹ Kachler, J., *Justus Liebigs Ann. Chem.*, 1879, **197**, 86.

¹⁰ Reychler, A., *Ber. Dtsch. Chem. Ges.*, 1896, **29**, 697.

¹¹ Wagner, G., and Brickner, W., *Ber. Dtsch. Chem. Ges.*, 1899, **22**, 2302.

¹² Pelter, A., and Harper, S. H., in 'Rodd's Chemistry of Carbon Compounds' (Ed. S. Coffey) 2nd Edn, Vol. II^c, pp. 160, 229 (Elsevier: Amsterdam 1969).

(<20°), a drop of tetramethylsilane added, and the ^1H n.m.r. spectrum recorded, all as rapidly as possible. ^1H n.m.r. (CHCl_3) δ 2.40, br s, H4; 1.85, br s, H1; 1.59, s, 3-Me; 1.20, s, *exo*-2-Me; 0.98, s, *endo*-2-Me. No peaks attributable to isoborneol (4), isobornyl chloride (3)¹³ or bornyl chloride (6) were observed. After 30 min at 25°, n.m.r. peaks for isomer (3) became visible at δ 3.88, q, H2; 1.08, 0.98, 0.86, 3s, Me. After 7 h the two compounds (1) and (3) were *c.* 50:50, while after 48 h no peaks for compound (1) remained.

Evaporation to dryness (<20°) of a portion of the original chloroform solution gave colourless crystals with a ^1H n.m.r. spectrum (CCl_4) identical with that recorded⁷ for compound (1). The crystals in cold pentane deposited crystals which showed increasing amounts of rearranged chloride (3) (by n.m.r.).

Camphene in chloroform at 0° with hydrogen chloride gas for 4 h gave, for comparison purposes, a mixture (*c.* 50:50) of camphene hydrochloride (1) and isobornyl chloride (3).

Borneol (5) with phosphorus pentachloride, as above, showed camphene hydrochloride (1) (90%), isobornyl chloride (3) (5%) and unchanged borneol (5) (5%).

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¹³ Flautt, T. J., and Erman, W. F., *J. Am. Chem. Soc.*, 1963, **85**, 3212.