The 3-Chloro(methyl)cyclopentyl Cation and its Reaction with Carbon Monoxide. The Ionization Mechanism of *trans*-1,2-Dichlorocyclohexane in Super Acid (FSO_3H–SbF_5)

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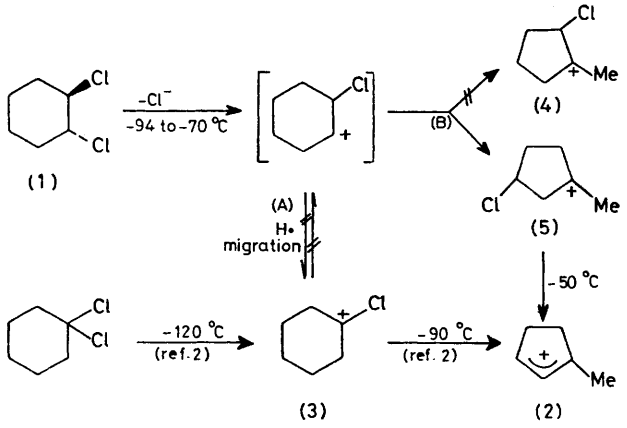
Summary The title ion (**5**) was identified as the intermediate in the ionization of *trans*-1,2-dichlorocyclohexane in super acid solution; it is stable to about −50 °C and it is attacked by CO at −78 °C predominantly (93:7) *cis* to the chlorine substituent.

IONIZATION of *trans*-1,2-dichlorocyclohexane (**1**) in super acid at −60 °C was reported to give the 1-methylcyclopentenyl cation (**2**) as the only observable product.[1] However, there are at least two conceivable pathways for the formation of this cation (**2**): (A) *via* the known[2] 1-chloro-

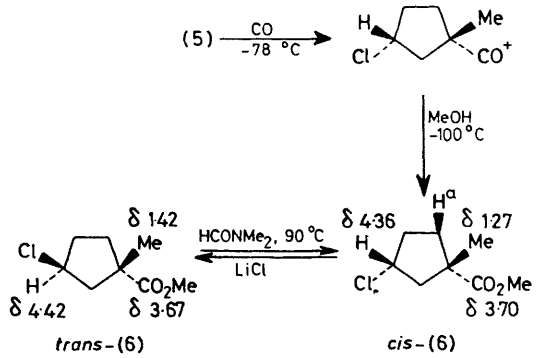
cyclohexyl cation (**3**), and (B) *via* the 2-chloro-(**4**) or 3-chloro-(methyl)cyclopentyl cation (**5**).

In the present study, careful ionization[3] of (**1**) in FSO_3H–SbF_5 (4:1) at −94 to −70 °C led to a species identified as (**5**) by its ^1H n.m.r. spectrum:[4] δ 5·43 (1H), 4·80 and 4·27 (partially overlapped, integrating together for 7H, the lower field signal being broader and larger than the higher field signal), and 3·19 (2H). The isomeric ion (**4**) and other possible carbocations or chloronium ions[5] were not compatible with the observed spectrum. Thus, ionization of (**1**) follows path (B).



Under the conditions of our experiments,[3] formation of (**2**) (from **5**) occurred with significant speed only above −50 °C (half-life *ca.* 10 min at −45 °C). At −70 °C (**5**) was stable in solution for several hours.

For positive identification the solution of (**5**) was treated with carbon monoxide (1·5 MPa, 2·75 h, −78 °C), then quenched in methanol at −100 °C to give the ester (**6**) (yield 92% by g.l.c.) as a 93:7 mixture of *cis* and *trans* isomers,† purified by column chromatography (silica gel Woelm, pentane-ether, 9:1 as eluent).‡ The stereoisomers were incompletely separated on a non-polar, silicone DC-200 g.l.c. column, but were well separated on a polar, Carbowax 20M column, the less polar *trans*-(**6**) (7%) being eluted first. G.l.c.–mass spectra of the two isomers were virtually the same, with *M* at *m/e* 178/176 and the expected fragments. Other spectral data for *cis*-(**6**) [in the 93:7 mixture with *trans*-(**6**)] were: ν_{max} (neat) 1740 cm^{-1}; ^1H n.m.r. ($CDCl_3$, Me_4Si; 100 MHz) δ 4·36 (1H, quintuplet, *J* 6 Hz, CHCl[6]), 3·70 (3H, s, OMe), 2·30—2·65 (2H, m), 1·80—2·27 (3H, m), 1·40—1·70 (1H, m, H^a), and 1·27 (3H, s, Me);§ ^{13}C n.m.r. ($CDCl_3$, Me_4Si) δ 26·1 (Me), 35·4 (CH_2), 36·5 (CH_2), 47·9 (CH_2, C-2), 48·2 (C-1), 52·1 (Me), and 59·4 (CH, C-3) p.p.m. The observed ^{13}C chemical shifts match well the values calculated for (**6**) based on additivity of substituent effects,[7] but not the values calculated for the ester derived from the cation (**4**).



Treatment of the original ester with LiCl in dimethylformamide for 3·5 h at 90 °C led to epimerization at C-3 in (**6**). Further warming for another 1·25 h failed to change significantly the isomer ratio (*cis*:*trans* 52:48 by g.l.c.). The ^1H n.m.r. spectrum ($CDCl_3$) of *trans*-(**6**) differed in the expected way[8] from the spectrum of its stereoisomer: δ 1·42 (Me), 1·67—2·89 (CH_2's), 3·67 (OMe), and 4·42 (*J* 6 Hz, CHCl) p.p.m.¶

It appears, rather unexpectedly, that (**5**) is attacked by CO from the most hindered side.

(*Received*, 14*th February* 1977; *Com.* 126.)

† *cis* and *trans* refer to the relative positions of the Cl and CO_2Me substituents.

‡ The chromatographed material was > 98% pure (g.l.c.), while the isomer ratio was not altered. The unpurified material darkened considerably on standing. The same behaviour was observed for methyl 1-methylcyclopentanecarboxylate prepared similarly from the 1-methylcyclopentyl cation.

§ For comparison, methyl 1-methylcyclopentanecarboxylate had δ(OMe) 3·65 and δ(Me) 1·24.

¶ The values are obtained by subtracting the spectrum of *cis*-(**6**) from the spectrum of the 52:48 mixture.

[1] G. A. Olah, G. Liang, and Y. K. Mo, *J. Amer. Chem. Soc.*, 1972, **94**, 3544.
[2] G. A. Olah, G. Liang, and Y. K. Mo, *J. Org. Chem.*, 1974, **39**, 2394.
[3] D. Fărcaşiu and L. Craine, *J.C.S. Chem. Comm.*, 1976, 687. It should be emphasized that we used a 4:1 molar ratio of FSO_3H to SbF_5, while in ref. 1 a 1:1 mixture was used. Thus, the rearrangement of the cyclohexenyl cation to the 1-methylcyclopentenyl cation was observed by us in 4:1 FSO_3H–SbF_5, but was not observed in 1:1 FSO_3H–SbF_5 (G. A. Olah, personal communication).
[4] For appropriate models see: G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *J. Amer. Chem. Soc.*, 1967, **89**, 2692; G. A. Olah and J. Lukas, *ibid.*, p. 2227; G. A. Olah, J. M. Bollinger, Y. K. Mo, and J. Brinich, *ibid.*, 1972, **94**, 1164; D. M. Brouwer, *Rec. Trav. chim.*, 1968, **87**, 210.
[5] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, 1968, **90**, 947; (b) G. A. Olah and P. E. Peterson, *ibid.*, p. 4675; G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, p. 6988; S. P. McManus and P. E. Peterson, *Tetrahedron Letters*, 1975, 2753, and references therein.
[6] The spectrum of chlorocyclopentane shows a similar splitting pattern for the CHCl signal (δ 4·35): Sadtler Catalog of NMR Spectra No. 6229.
[7] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972.
[8] Compare with *cis*- and *trans*-1,5,5-trimethyl-3-hydroxycyclopentanecarboxylic acid: J. W. Faigle, H. Müller, W. von Philipsborn, and P. Karrer, *Helv. Chim. Acta*, 1964, **81**, 741.