Transannular Interactions in the Chlorination of *cis,cis*-Cyclo-octa-1,5-diene and *cis*-Cyclo-octene with $SbCl_5$

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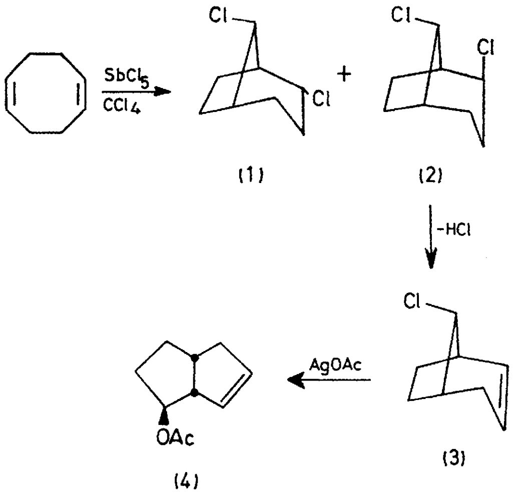
Summary The chlorinations of *cis,cis*-cyclo-octa-1,5-diene and *cis*-cyclo-octene with $SbCl_5$ in CCl_4 give *endo*- and *exo*-2-*anti*-8-dichlorobicyclo[3,2,1]octanes and *cis*- and *trans*-1,4-dichlorocyclo-octanes respectively in 70—80% yield.

It has recently been reported that $SbCl_5$ is a good reagent for the *cis*-chlorination of simple olefins[1,2] and for the formation of *cis*-1,4-dichlorobut-2-ene from butadiene.[2,3] We now describe the unusual chlorinations of *cis,cis*-cyclo-octa-1,5-diene [1,5-COD] and *cis*-cyclo-octene with $SbCl_5$, both involving a transannular interaction.

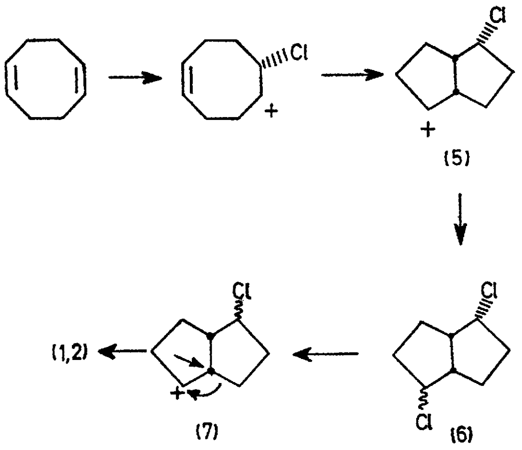
When $SbCl_5$ in CCl_4 was slowly added to a CCl_4 solution of 1,5-COD at −20°, an isomeric mixture of *endo*-2-*anti*-8-dichlorobicyclo[3,2,1]octane (**1**) and *exo*-2-*anti*-8-dichlorobicyclo[3,2,1]octane (**2**) was obtained in 70% yield [(**1**) : (**2**) = *ca.* 7 : 3 by g.l.c.] (Scheme 1). A mixture of (**1**) and (**2**) (b.p. 76—78° at 4 Torr) was analysed as $C_8H_{12}Cl_2$, did not have any absorption due to olefinic protons in its i.r. and n.m.r. spectra, did not decolourize bromine in CCl_4, and was monodehydrochlorinated to bicyclo[3,2,1]oct-2-en-*anti*-8-yl chloride (**3**) by treatment with Bu^{t}OK in DMSO [**3**; b.p. 78—81° at 22 Torr, *m/e* 142(M^+), δ (CCl_4) 1·2—2·8 (m, 8H), 4·23 (s, 1H), 5·2—6·0 (m, 2H)]. (**2**) was more readily dehydrochlorinated than (**1**) as expected from *E*2 elimination,[4] since the chlorine, two carbons (C-2 and C-3) and the hydrogen on C-3 lie in a common plane in (**2**). By this procedure (**1**) was separated from (**2**) [**1**; b.p. 123—124° at 25 Torr, *m/e* 178 (M^+), δ (CCl_4) 1·2—2·7 (m, 10H), 3·85 (s, 1H), 3·85—4·1 (m, 1H)]. A sharp singlet at δ 3·85 in (**1**) and at δ 4·23 in (**3**) could be assigned to a *syn*-hydrogen at C-8 the absorption being very similar to that of *endo*-2-methoxymethylbicyclo[3,2,1]oct-*anti*-8-yl chloride[5] [δ (CCl_4) 3·94, singlet]. Additional proof for the structure of (**3**) was obtained by its reaction with silver acetate in acetic acid which gave *exo-cis*-bicyclo[3,3,0]oct-7-en-2-yl acetate (**4**) [b.p. 101—102° at 18 Torr, *m/e* 166 (M^+), lit.[6] b.p. 69—73° at 5 Torr]. LeBel and Spurlock[7] have reported that (**4**) was formed by the acetolysis of the *p*-toluenesulphonate analogue of (**3**).



SCHEME 1

The transannular cyclization of 1,5-COD usually gives bicyclo[3,3,0]octane derivatives. The formation of bicyclo[3,2,1]octane derivatives has been reported only in the case of the reaction with $MeOCH_2Y$ (Y = OAc, Cl, and OMe), and even in this case the main products were bicyclo[3,3,0]octane derivatives.[5] Although the exact pathway for the formation of (**1**) and (**2**) is not yet clear, one possibility is that a mixture of *endo*-2,6- and *endo,exo*-2,6-dichlorobicyclo[3,3,0]octanes (**6**) is formed at first through the cation (**5**) (*endo*-Cl) and then isomerized rapidly to a mixture of (**1**) and (**2**) by $SbCl_5$ catalyst through the cation (**7**) (*exo*- and *endo*-Cl) (Scheme 2). We have already shown that $SbCl_5$ is a very effective catalyst for such isomerization between the isomeric dichloronorbornanes.[8]

The chlorinations of 1,5-COD with other chlorinating agents such as PCl_5, SO_2Cl_2, $PhICl_2$, $CuCl_2$, $SeCl_4$, $MoCl_5$, and $PbCl_4$ gave a mixture of *cis*- and *trans*-5,6-dichlorocyclo-octenes and none of (**1**) and (**2**).



SCHEME 2

Application of this chlorination to *cis*-cyclo-octene at −30° resulted in the preferable formation of an isomeric mixture of 1,4-dichlorocyclo-octanes (78% yield; *cis*:*trans* =93:7; b.p. 115—118° at 8 Torr, lit.[9] b.p. 116—119° at 10 Torr) together with a 3% yield of the *cis*-1,2-isomer. It was confirmed that no interconversion occurred between the 1,2- and 1,4-isomers and also between the *cis*- and *trans*-1,4-isomers under the present conditions. The reaction apparently involves a transannular 1,5-hydrogen shift and the fact that the selectivity for the *cis*-1,4-isomer is quite high may be explained by assuming the presence of the hydrogen-bridged chlorocyclo-octyl cation intermediate, almost the same as proposed in the formolysis of *cis*-cyclo-octene oxide.[10] 1,4-Chlorination has also been reported in the reaction with $PbCl_4$[9] and we found that it also occurred with $PhICl_2$, VCl_4 and $SeCl_4$ although the selectivity and yield was low compared to $SbCl_5$ and $PbCl_4$. Chlorinations with $CuCl_2$, PCl_5, and SO_2Cl_2 gave only the 1,2-isomer.

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[1] S. Uemura, O. Sasaki, and M. Okano, *Chem. Comm.*, 1971, 1064; F. Akiyama, T. Horie, and H. Matsuda, *Bull. Chem. Soc. Japan*, 1973, **46**, 1888.

[2] S. Uemura, A. Onoe, and M. Okano, *Bull. Chem. Soc. Japan*, 1974, **47**, 692.

[3] R. P. Vignes and J. Hamer, *J. Org. Chem.*, 1974, **39**, 849.

[4] E. S. Gould in 'Mechanism and Structure in Organic Chemistry,' Holt, Rinehart, and Winston, New York, 1959, p. 484.

[5] I. Tabushi, K. Fujita, and R. Oda, *J. Org. Chem.*, 1970, **35**, 2376.

[6] K. Fujita, K. Hata, R. Oda, and I. Tabushi, *J. Org. Chem.*, 1973, **38**, 2640.

[7] N. A. Lebel and L. A. Spurlock, *Tetrahedron*, 1964, **20**, 215.

[8] S. Uemura, A. Onoe, and M. Okano, submitted for publication.

[9] P. W. Henniger, L. J. Dukker, and E. Havinga, *Rec. Trav. chim.*, 1966, **85**, 1177.

[10] Ref. 4, p. 600.