A Stereospecific Rearrangement of ββ-Dichlorocyclobutanols to α-Chlorocyclopropane Carboxaldehydes

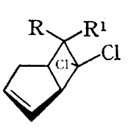
By P. R. BROOK

(*Department of Organic Chemistry, The University, Leeds* 2)

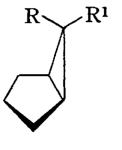
THE addition of dichloroketen to olefines provides a useful source of αα-dichlorocyclobutanones.[1–3] The stereospecific rearrangement of cyclobutanols derived from one of these adducts, that from cyclopentadiene, is now reported. The reaction yields α-chlorocyclopropane carboxaldehydes, and, apart from its general synthetic utility, is an example of conformation and stereoelectronic control in cyclobutane derivatives.

The cyclobutanols were obtained by the reduction of the adduct, 7,7-dichlorobicyclo[3,2,0]hept-2-en-6-one,[2] with sodium borohydride. The mixture of the *endo*-alcohol (I; m.p. 34°) and the *exo*-alcohol (II; m.p. 81°), formed in the ratio of 81 : 19, were separated by chromatography (Kieselgel G)[4] or by preparative g.l.c. Stereochemical assignments made were based on the n.m.r. spectra of the alcohols and their derivatives:[†] in particular the signal of the C-6 hydrogen atom was at a higher field in *exo*-derivatives (shielding by the bonds of the five-membered ring), and the relative chemical shifts of the two hydrogen atoms on C-4 were further apart in the *endo*-derivatives (greater deshielding of C-4 *endo*-hydrogen by the substituent). The larger proportion of *endo*-alcohol (I) is consistent with preferred approach of borohydride ion from the less hindered *exo*-face of the bicyclic ketone.

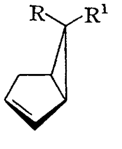
Catalytic reduction of the double bond in these bicyclic alcohols (Pt–H$_2$ in MeOAc) gave the dihydro-derivatives [dihydro-(I), m.p. 51°; dihydro-(II); m.p. 81°]. It was convenient to use the products of rearrangement of these saturated alcohols to prove the formation of the bicyclo[3,1,0]hexane skeleton. For clarity, the stereochemistry of the reaction is assumed at this stage, although proof was only obtained by rearrangement of the unsaturated alcohols (I and II; see below).



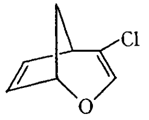
	R	R^1
(I)	OH	H
(II)	H	OH



	R	R^1
(III)	Cl	CHO
(IV)	CHO	Cl
(V)	Cl	CO$_2$H
(VI)	CO$_2$H	Cl
(VII)	CO$_2$H	H
(VIII)	H	CO$_2$H



	R	R^1
(IX)	Cl	CHO
(X)	CHO	Cl
(XI)	Cl	CO$_2$H

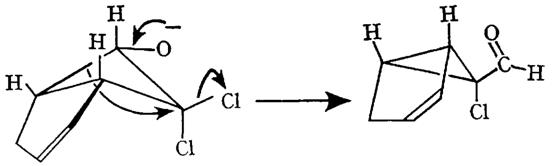


(Xa)

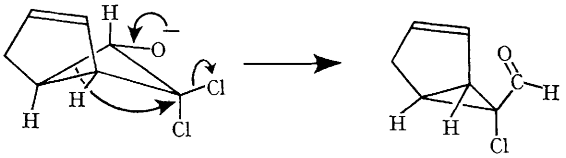
[†] Attempts to form the strained iodo-ether (NaHCO$_3$–I$_2$) failed with both *endo*- and *exo*-alcohols. In the former case the crude product was a cyclobutanone (ν_{max} 1800 cm.$^{-1}$), which suggested that no skeletal rearrangement had occurred in the reduction of the bicycloheptenone.

In the *endo*-series [dihydro-(I)], treatment with aqueous base (2N-NaOH) gave the *exo*-carboxaldehyde (III; 70%) which with silver oxide gave the corresponding α-chloro-acid (V; m.p. 103—104°; pK_a in water, 3·05 ± 0·11). Similarly, *exo*-alcohol [dihydro-(II)] gave the *endo*-carboxaldehyde (IV), and thence the related α-chloro-acid (VI; m.p. 118—120°; pK_a in water, 2·86 ± 0·03). Reductive dechlorination of either chloro-acid (Na–liq. NH_3) gave the same mixture of known *endo*- and *exo*-bicyclo[3,1,0]hexane-6-carboxylic acids [respectively (VII) and (VIII); ratio 69 : 31]. This shows that the same radical and/or carbanion[6] is formed from either α-chloro-acid. The stability of such species is expected in view of the difficulty of the (predicted[7]) conrotatory opening to a less strained allylic isomer, and, in addition, the presence of the α-carboxylate anion. Preponderance of the *endo*-acid (VII) indicates preferential protonation of the carbanion from the less hindered *exo*-face.

(I) *endo*-series



(II) *exo*-series



The relative configuration of the rearrangement products, assumed above, has been assigned from the results obtained in the unsaturated series. *exo*-Alcohol (II), when treated with base as above, gave exclusively the *endo*-carboxaldehyde (X, 40%), having the correct analysis figures, but, from its spectroscopic properties, clearly existing largely (~95%) as the valence bond tautomer (Xa).[8] This equilibrium can only exist if the double bond and carboxaldehyde groups are on the same side of the cyclopropane ring.‡

Similarly, the *endo*-alcohol (I) gave the *exo*-carboxaldehyde (IX; no valence bond tautomer possible) and from this the corresponding *exo*-acid (XI; m.p. 115°). When this acid was melted or crystallised from hot water a smooth conversion into benzoic acid ensued, by loss of the elements of hydrogen chloride. This strongly suggests that the chlorine atom in the acid (XI) has the *endo*-configuration, and the opening of the cyclopropane ring to the allyl cation involves rearward attack by the electrons of the 1,5-bond on the C-6, Cl bond with disrotatory opening of the ring (C-1 and C-5 outward).[9]

Proof that the rearrangement of the *endo*-alcohol (I) and its dihydro-derivative followed the same stereochemical course was obtained by reduction of chloro-acid (XI) to its dihydro-derivative, identical with the acid (V) obtained from the saturated *endo*-alcohol [dihydro-(I)].

Ring contractions of cyclobutanes to cyclopropane derivatives usually involve non-classical bicyclobutonium ions.[10] Wiberg has shown that when the cyclobutane is held in a non-planar conformation neighbouring group participation by a cyclobutane bond requires the leaving group to be pseudo-equatorial,[11,12] This stereoelectronic requirement has been assumed in other cases of ring-opening[13] or ring-contraction[14] of cyclobutanes.

In the present ring-contraction, there is some evidence that carbonium ions are not involved: the alcohols are unaffected by neutral aqueous silver ion, and strong base appears to be necessary for reaction. Development of partial positive charge at C-7 by ionisation of one chloro-group would be discouraged by the inductive effect of the second one. It is suggested that a concerted reaction occurs as in equations (1) and (2), with the 'push' of the cyclobutoxide ion providing a greater driving force than the 'pull' of the chlorine atom. Participation by the cyclobutane 5,6-bond requires the hydroxyl group and the chlorine atom to be both pseudo-equatorial and *trans* to obtain maximum orbital overlap in the rearrangement. The reaction

‡ It is noteworthy that the equilibrium in this case is in favour of the 2-oxabicyclo[3,2,1]octa-3,6-diene (Xa), whereas the compound without the chlorine (ref. 8) exists mainly as the bicyclo[3,2,1]hex-2-en-6-*endo*-carboxaldehyde (70%). The chlorine atom would be expected to destabilise the carboxaldehyde (X) by inductive effect (*cf.* chloral) and stabilise the form (Xa) by extra resonance as a vinylic chloride.

can be compared with the conversion of *trans*-2-chlorocyclohexanol into cyclopentane carboxaldehyde[15] (which has a different driving force, however).

(*Received, March 12th*, 1968; *Com.* 304.)

[1] H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, 1965, **87**, 5257.

[2] L. Ghosy, R. Montaigne, and P. Mollet, *Tetrahedron Letters*, 1966, 135.

[3] R. W. Turner and T. Sedam, *Chem. Comm.*, 1966, 399.

[4] B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.

[5] J. Meinwald, S. S. Labone, and M. S. Chadha, *J. Amer. Chem. Soc.*, 1963, **85**, 582.

[6] H. Smith, "Chemistry in Non-aqueous Ionising Solvents", vol. I, part 2, "Organic Reactions in Liquid Ammonia", Interscience, New York, p. 196.

[7] (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395; (b) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, p. 2045.

[8] M. Rey and A. S. Dreiding, *Helv. Chim. Acta.*, 1965, **48**, 1985.

[9] (a) U. Schöllkopf, K. Fellenberger, N. Patsch, P. von R. Schleyer, T. Su, and G. W. van Dine, *Tetrahedron Letters*, 1967, 3639; (b) M. S. Baird and C. B. Reese, *ibid.*, p. 1379.

[10] (a) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1959, **81**, 4390; (b) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, 1960, **11**, 171.

[11] K. B. Wiberg and R. Fenoglio, *Tetrahedron Letters*, 1963, 1273.

[12] K. B. Wiberg and B. A. Hess, *J. Amer. Chem. Soc.*, 1968, **89**, 1967.

[13] (a) C. F. Wilcox and D. L. Llealy, *J. Org. Chem.*, 1963, 3450; (b) C. F. Wilcox and R. J. Engen, *Tetrahedron Letters*, 1966, 2759.

[14] K. B. Wiberg and J. A. Ashe, tert., *J. Amer. Chem. Soc.*, 1968, **89**, 63. (Ref. work of Nelson and Goering, Ph.D. Thesis, University of Wisconsin, 1960.)

[15] M. Godchot, M. Mousseron, and R. Grainger, *Compt. rend.*, 1935, **200**, 748.