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Ring Expansion of Bicyclic *gem*-Dihalo- and Monohalocyclopropanes

Teiichi Ando, Hirokazu Hosaka, Hiroki Yamanaka and Wataru Funasaka

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

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Some bicyclic *gem*-dichlorocyclopropanes (Ia through Id) and *gem*-chlorofluorocyclopropanes (IIa through IId) were prepared by the addition of dichloro- and chlorofluorocarbene, respectively, to the appropriate cyclic olefins. The reduction of these dihalocyclopropanes with tri-*n*-butyltin hydride gave the corresponding monochloro- (IIIa through IIId) or monofluorocyclopropanes (IVa through IVd) in fairly good yields. When treated with an excess of hot quinoline, the *endo*-chloro isomers of IIa, IIb, IId, IIIa, IIIb, and IIId were converted to their ring expansion products, whereas their *exo*-chloro isomers were recovered unchanged. In contrast, the *exo*-chloro isomers of IIc and IIIc decomposed more readily than their *endo*-chloro isomers under similar conditions. These results were discussed on the concept of a concerted disrotatory process.

The ring opening or ring expansion reactions of *gem*-dihalo- and monohalocyclopropanes have received much attention in recent years, and it has been found that the reaction rate is dependent not only on the kind of halogen[1] but also on the molecular geometry of the substrate.[2-9] Baird and Reese[2] have proved that *endo*-6-chlorobicyclo[3.1.0]hexane is converted to 3-chlorocyclohexene when heated at 120°C. Ghosez *et al.*,[3] have shown that the *endo*-chloro isomer of 3-chloro-8-oxatricyclo[3.2.1.0^{2,4}]octane undergoes ring expansion at 80°C, while the *exo*-chloro isomer remains unchanged after being heated at 150°C for 15 hr. Analogous results have been reported with the chlorofluorocarbene adduct to indene,[4] and the chloro-, bromo-, or chlorofluorocarbene adduct to norbornene.[5-7] Schweizer and Parham[8] showed that the *exo*-chloro isomer of 7-chloro-2-oxabicyclo[4.1.0]heptane decomposed at 120°C in quinoline to give 2,3-dihydroöxepin, while the *endo*-chloro isomer remained unchanged at 176.5°C in quinoline.

This paper describes the synthesis of a series of *n*,*n*-dichloro-, *n*-chloro-*n*-fluoro-, *n*-chloro-, and *n*-fluorobicyclo[*n*−3.1.0]alkanes (n=6, 7, and 9) and their 2-oxa analogues (n=7) and the stereospecificity observed in some of their ring expansion reactions in quinoline. A part of the present work has already been reported in preliminary communications.[9,10)]

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[1] P. S. Skell and S. R. Sandler, *J. Am. Chem. Soc.*, **80**, 2024 (1958).

[2] M. S. Baird and C. B. Reese, *Tetrahedron Letters*, **1967**, 1379.

[3] L. Ghosez, P. Laroche and G. Slinckx, *ibid.*, **1967**, 2767.

[4] W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **22**, 730 (1957).

[5] C. W. Jefford, E. Huang-Yen and R. T. Medary, *Tetrahedron Letters*, **1966**, 6317.

[6] C. W. Jefford and R. T. Medary, *Tetrahedron*, **23**, 4123 (1967).

[7] L. Ghosez, G. Slinckx, M. Glineur, R. Hoet and P. Laroche, *Tetrahedron Letters*, **1967**, 2773.

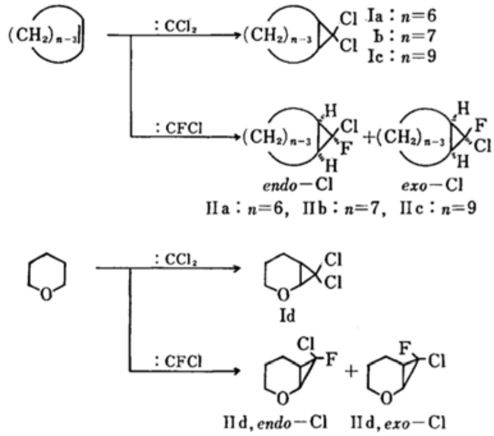
[8] E. E. Schweizer and W. E. Parham, *J. Am. Chem. Soc.*, **82**, 4085 (1960).

[9] T. Ando, H. Yamanaka and W. Funasaka, *Tetrahedron Letters*, **1967**, 2587.

[10] T. Ando, H. Yamanaka, S. Terabe, A. Horike and W. Funasaka, *ibid.*, **1967**, 1123.

Results and Discussion

Synthesis of n,n-Dichloro- and n-Chloro-n-fluorobicyclo[$n-3.1.0$]alkanes ($n=6$, 7, and 9) and Their 2-Oxa Analogues ($n=7$). 6,6-Dichlorobicyclo[3.1.0]hexane (Ia), 7,7-dichlorobicyclo[4.1.0]heptane (Ib), 9,9-dichlorobicyclo[6.1.0]nonane (Ic), and 7,7-dichloro-2-oxabicyclo[4.1.0]heptane (Id) were prepared by the reaction of dichlorocarbene with cyclopentene, -hexene, -octene, and 2,3-dihydro-4*H*-pyran, respectively. The corresponding chlorofluoro derivatives (IIa, IIb, IIc, and IId) were prepared similarly from chlorofluorocarbene. The dihalocarbenes were generated very conveniently by gradual addition of methanol to a mixture of sodium hydride and methyl trichloro- or dichlorofluoroacetate, which generally gave better yields of the dihalocarbene adducts than the conventional sodium methoxide - trihaloacetate method.[11,12] The yields and the properties of the *gem*-dihalocyclopropanes thus prepared are summarized in Table 1.

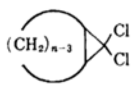
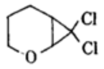
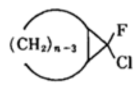
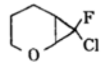


As is shown in Table 1, each of the chlorofluoro derivatives obtained was a mixture of the *endo*-chloro and the *exo*-chloro isomers, with the former predominating. Similar results have been reported in the addition of chlorofluorocarbene to other olefins.[13a] Probably, as Moss and Gerstl pointed out,[13] the electronic factor (difference in polarizability of the halogen substituent) plays a more important role than the steric factor in determining the stereoselectivity of the dihalocarbene addition.

The assignments of the configuration were made by NMR spectroscopy, based on the generalization that in fluorocyclopropanes $J_{\mathrm{HF},cis}$ is larger than $J_{\mathrm{HF},trans}$[14] and that cyclopropyl fluorines are shielded by *cis*-, and deshielded by *trans*-, alkyl groups.[9,13] Their NMR data are given in Tables 2 and 3.

Synthesis of n-Chloro- and n-Fluorobicyclo[$n-3.1.0$]alkanes ($n=6$, 7, and 9) and Their 2-Oxa Analogues ($n=7$). 6-Chlorobicyclo[3.1.0]hexane (IIIa), 7-chlorobicyclo[4.1.0]heptane (IIIb), 9-chlorobicyclo[6.1.0]nonane (IIIc), and 7-chloro-2-oxabicyclo[4.1.0]heptane (IIId) were prepared, as a mixture of the *endo*-chloro and the *exo*-chloro isomers, by partially reducing the corresponding dichloro derivatives (Ia, Ib, Ic, and Id) with an equimolar amount of tri-n-butyltin hydride in the

TABLE 1. SYNTHESIS AND PROPERTIES OF n,n-DICHLORO- AND n-CHLORO-n-FLUOROBICYCLO[$n-3.1.0$]-ALKANES ($n=6$, 7, AND 9), AND THEIR 2-OXA ANALOGUES ($n=7$)

Structure	n	Yield (%)	Isomer ratio (*endo*-Cl/*exo*-Cl)	Bp (°C/mmHg)	n_D (°C)
	6 (Ia)	55		60—62/15	1.5910 (22)
	7 (Ib)	65		72—74/12	1.5003 (23)
	9 (Ic)	55		80—83/3.5	1.5006 (31)
	(Id)	70		72—73/8	1.4967 (24)
	6 (IIa)	44	2.3—2.4	50—53/43	1.4495 (16)
	7 (IIb)	60	1.2—1.5	50—52/15	1.4560 (20)
	9 (IIc)	51	1.9—2.0	70—73/8	1.4660 (31)
	(IId)	78	1.5—1.6	68—69/20	1.4556 (20)

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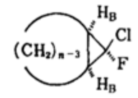
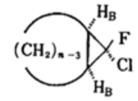
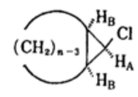
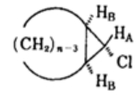
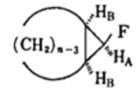
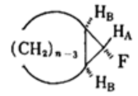
[11] W. E. Parham and F. C. Loew, *J. Org. Chem.*, **23**, 1705 (1958).

[12] R. A. Moore and R. Levine, *ibid.*, **29**, 1883 (1964).

[13] a) R. A. Moss and R. Gerstl, *ibid.*, **32**, 2268 (1967). b) R. A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967).

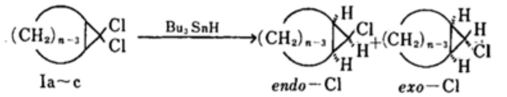
[14] a) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **40**, 875 (1962). b) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962). c) D. J. Patel, M. E. H. Howden and J. D. Roberts, *ibid.*, **85**, 3218 (1963). d) K. L. Williamson, Y. Li, F. H. Hall and S. Swager, *ibid.*, **88**, 5678 (1966).

TABLE 2. PARAMETERS OF NMR SPECTRA OF *n*,*n*-DIHALO- AND *n*-HALOBICYCLO[$n-3.1.0$]-ALKANES (n=6, 7, AND 9)

Structure	n	Chemical shift, ppm		Coupling constant, Hz		
		H_A^*	F**	J_{H_AF}	J_{H_BF}	$J_{H_AH_B}$
	6		47.5		19.2	
	7		47.8		19.0	
	9		46.4		15.8	
	6		82.8		8.1	
	7		82.3		5.0	
	9		83.9		7.1	
	6	3.34				7.5
	7	3.22				7.5
	9	3.10				7.5
	6	2.67				1.4
	7	2.70				3.3
	9	2.30				2.5
	6	4.62	158.0	66.3	10.0	6.5
	7	4.47	156.0	68.0	9.0	6.3
	9	4.32	164.0	64.8	6.0	6.0
	6	4.23	137.0	64.3	21.0	1.0
	7	4.25	126.2	65.0	18.0	2.0
	9	3.72	129.3	62.4	19.7	1.0

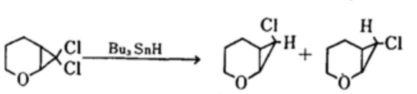
* Downfield from TMS.
** Upfield from trifluoroacetic acid.

presence of azobisisobutyronitrile.[15] The yields and the properties of the chlorocyclopropanes thus prepared are shown in Table 4, together with the isomer ratios determined by gas chromatography (glpc) before distillation.



Ia~c endo−Cl exo−Cl

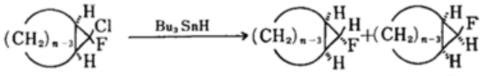
IIIa : n=6, IIIb : n=7, IIIc : n=9



Id IIId, endo−Cl IIId, exo−Cl

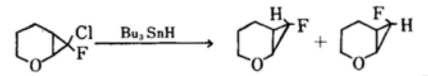
It is to be noted that the *endo*-chloro isomer predominates in IIIb and IIIc, whereas the *exo*-chloro isomer predominates in IIIa.[16]

Under similar conditions, an isomeric mixture of IIa was converted to a mixture of the *endo*-fluoro and the *exo*-fluoro isomers of 6-fluorobicyclo[3.1.0]-hexane (IVa). 7-Fluorobicyclo[4.1.0]heptane (IVb), 9-fluorobicyclo[6.1.0]nonane (IVc), and 7-fluoro-2-oxabicyclo[4.1.0]heptane (IVd) were obtained, as a mixture of isomers, from IIb, IIc, and IId, respectively. The reduction of these chlorofluorocyclopropanes required a longer reaction time than that of the corresponding dichlorocyclopropanes, and there was no sign of the monochloro derivative being formed. The yields and the properties of the products are shown in Table 5, together with the isomer distributions.



IIa~c exo−F endo−F

IVa : n=6, IVb : n=7, IVc : n=9



IId IVd, exo−F IVd, endo−F

A comparison of Tables 1 and 5 reveals that the isomer ratio of the reduction product (IVa, IVb, and IVc) is quite close to that of the starting material (IIa, IIb, and IIc, respectively). This result is best explained by the stereospecific nature of the reduction of *gem*-halofluorocyclopropanes by organotin hydrides, which has already been demonstrated with IIa and IIb by isolating the pure isomers and reducing them separately.[17] In contrast, the reduction of IId did not occur stereospecifically, as is suggested by the disagreement of the isomer ratio of IVd with that of IId. The nonstereospecific nature of the reduction has been demonstrated by reducing the pure *endo*-chloro isomer of IId,[18] and will be discussed in a separate paper.

The configurations of the isomers of the chloro- and fluorocyclopropanes thus prepared were determined by their NMR spectra; in addition to the generalizations quoted above, use was made of the rule that $J_{HH,cis}$ is generally larger than $J_{HH,trans}$ in cyclopropanes.[19] The NMR data are presented in Tables 2 and 3. The NMR spectra of IId, IIId, and IVd were analyzed by the double resonance method.[20]

Ring Expansion of *n*,*n*-Dichloro- and *n*-Chloro-*n*-fluorobicyclo[*n*−3.1.0]alkanes (*n*=6,

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[15] D. Seyferth, H. Yamazaki and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

[16] The predominant formation of the *exo*-halo isomer has been observed also in the reduction of 6,6-dichloro-3-oxabicyclo[3.1.0]hexane (prepared from 2,5-dihydrofuran and dichlorocarbene) with tri-*n*-butyltin hydride; H. Yamanaka, T. Ando and W. Funasaka, unpublished.

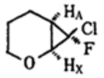
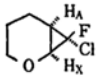
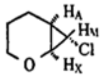
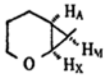
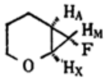
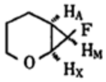
[17] T. Ando, F. Namigata, H. Yamanaka and W. Funasaka, *J. Am. Chem. Soc.*, **89**, 5719 (1967).

[18] T. Ando, H. Yamanaka and W. Funasaka, unpublished.

[19] W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967), and the references cited therein.

[20] We thank Dr. M. C. Woods, Dept. of Chemistry, Tohoku Univ., for his measurements of proton NMR spectra at 100 MHz and his valuable discussion.

Table 3. Parameters of NMR spectra of 7-chloro-7-fluoro-, 7-chloro-, and 7-fluoro-2-oxabicyclo[4.1.0]heptane

Structure	Chemical shift, ppm			Coupling constant, Hz					
	H^*_M	H^*_X	F**	J_{H_MF}	J_{H_AF}	J_{H_XF}	$J_{H_AH_M}$	$J_{H_AH_X}$	$J_{H_MH_X}$
			58.2		22	12			
			90.0		6	2			
	2.90	3.68					4.5	8.0	1.0
	3.01	3.68					8.4	7.8	5.0
	4.34	3.76	135.1	60.0	26.6	11.4	3.3	8.8	0
	4.29	3.28	165.0	6.33	1.23	0	6.7	8.2	4.3

* Downfield from TMS.
** Upfiled from trifluoroacetic acid.

Table 4. Synthesis and properties of *n*-chlorobicyclo[*n*—3.1.0]alkanes (*n*=6, 7, and 9) and 7-chloro-2-oxabicyclo[4.1.0]heptane

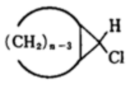
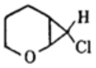
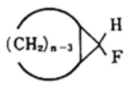
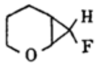
Structure	*n*	Reaction temp. (°C)	Yield (%)	Isomer ratio (*exo*-Cl/*endo*-Cl)	Bp (°C/mmHg)	n_D (°C)
	6 (IIIa)	80	82	1.6—1.7	65—70/63	1.4750 (21)
	7 (IIIb)	140	67	0.40—0.33	52—54/13	1.4860 (26)
	9 (IIIc)	90	72	0.45—0.46	77—79/8	1.4888 (31)
	(IIId)	85	67	1.0—1.3	40—45/4	1.4800 (24)

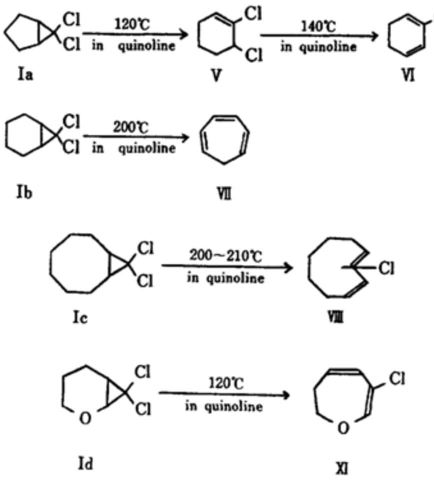
Table 5. Synthesis and properties of *n*-fluorobicyclo[*n*—3.1.0]alkanes (*n*=6, 7, and 9) and 7-fluoro-2-oxabicyclo[4.1.0]heptane

Structure	*n*	Reaction temp. (°C)	Yield (%)	Isomer ratio (*exo*-F/*endo*-F)	Bp (°C/mmHg)	n_D (°C)
	6 (IVa)	80	72	2.3—2.4	56—57/166	1.4234 (12)
	7 (IVb)	140	56	1.3—1.5	132—134/760	1.4400 (20)
	9 (IVc)	90	86	1.9—2.0	66—67/20	1.4519 (31)
	(IVd)	85	33	1.8—1.9	45—52/30	1.4383 (20)

7, and 9) and Their 2-Oxa Analogues (n=7). Recently, Lindsay and Reese[21] have found that the treatment of 7,7-dibromobicyclo[4.1.0]heptane with quinoline at 220—238°C gives 1,3,5-cycloheptatriene in 66—68% yield, while at 200°C under reduced pressure it gives a mixture of 1- and 2-bromo-1,3-cycloheptadiene in 38% yield. It has also been reported that 6,6-dibromobicyclo[3.1.0]-hexane or 6,6-dichlorobicyclo[3.1.0]hexane rearranges to the corresponding 2,3-dihalocyclohexene when heated at 150—180°C,[22] and that 7,7-dichlorobicyclo[4.1.0]heptane is converted to 1,3,5-cycloheptatriene when heated at 444—520°C.[23] These experimental results suggest that the thermal rearrangement of n,n-dihalobicyclo $[n-3.1.0]$ alkanes is often accompanied by dehydrohalogenation, and is assisted by the presence of a base such as quinoline.

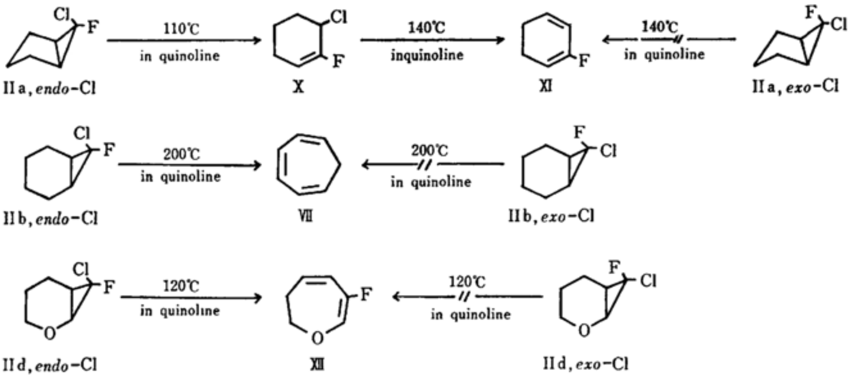
In accord with these findings, 6,6-dichlorobicyclo-[3.1.0]hexane (Ia) was converted to 2,3-dichlorocyclohexene (V) when heated at 120°C with an excess of quinoline. Further heating at 140°C resulted in the formation of 2-chloro-1,3-cyclohexadiene (VI). 7,7-Dichlorobicyclo[4.1.0]heptane (Ib) and 9,9-dichlorobicyclo[6.1.0]nonane (Ic) did not react at 120°C, and had to be heated at *ca.* 200°C in order to effect ring expansion. The products formed from Ib and from Ic were 1,3,5-cycloheptatriene (VII) and monochlorocyclononadiene (VIII),[24] respectively. Triene (VII) was probably formed *via* the intermediate chlorocycloheptadiene, which, however, could not be isolated under the reaction conditions. 7,7-Dichloro-2-oxabicyclo[4.1.0]heptane (Id) at 120°C in quinoline was converted to 2,3-dihydro-6-chloroöxepin (IX).

The lower temperature required for effecting the ring expansion of Ia, relative to that of Ib or Ic, may be due to the difference in ring strain between Ia (five-membered) and Ib or Ic (six- or eight-membered).



A similar ring expansion reaction occurred also when an isomeric mixture of 6-chloro-6-fluorobicyclo[3.1.0]hexane (IIa) was treated with quinoline at 110°C or at 140°C; 3-chloro-2-fluorocyclohexene (X) or 2-fluoro-1,3-cyclohexadiene (XI) were obtained, respectively. In these cases, the *exo*-chloro isomer was completely recovered. Similarly, the treatment of an isomeric mixture of 7-chloro-7-fluorobicyclo[4.1.0]heptane (IIb) and 7-chloro-7-fluoro-2-oxabicyclo[4.1.0]heptane (IId) with quinoline at 200°C or 120°C resulted in the formation of 1,3,5-cycloheptatriene (VII) and 2,3-dihydro-6-fluoroöxepin (XII), respectively, with complete recovery of the *exo*-chloro isomer. Fluorocycloheptadiene, the most probable precursor of VII in the ring expansion of IIb, was again not isolated.

These experimental facts indicate a much higher reactivity of the *endo*-chloro than that of the *exo*-chloro isomers. This stereospecificity, *i.e.*, the



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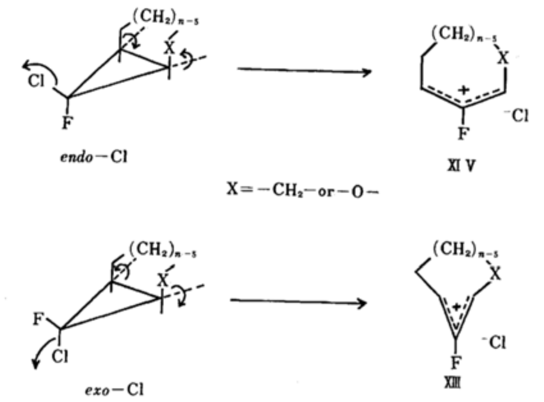
[21] D. G. Lindsay and C. B. Reese, *Tetrahedron*, **21**, 1673 (1965).

[22] a) J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **27**, 748 (1962). b) E. Bergman, *ibid.*, **28**, 2210 (1963).

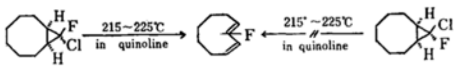
[23] a) H. E. Winberg, *ibid.*, **24**, 264 (1959). b) G. C. Robinson, *ibid.*, **29**, 3433 (1964).

[24] The structures of VIII, XV, and XVIII have not yet been fully established, but are only estimated; the results of their elemental analyses and their IR and NMR spectral data are in good agreement with the proposed structure (see Experimental), but the possibility that they might be a *cis*-diene or its derivative is not completely excluded.

strong dependence of the reaction rate upon the molecular geometry of the substrate, can be reasonably explained by assuming the rate-determining step of the ring opening of *gem*-chlorofluorocyclopropanes to be a "concerted disrotatory process,"[25] in which the chlorine is removed in preference to the fluorine, to form the corresponding 2-fluoroallyl cation. The selection rule advanced by DePuy *et al.*,[25] for such a process states that when the ring opening and the removal of the substituent occur simultaneously, the groups *trans* to the leaving group must rotate outward, and those *cis*, inward. If the same mechanism applies to the present reactions, the transition state (XIII) formed from the *exo*-chloro isomer of IIa, IIb, or IId would be sterically too much strained, as is shown below, for the ring expansion to occur. In contrast, the transition state (XIV) formed from the corresponding *endo*-chloro isomer would be much less strained.

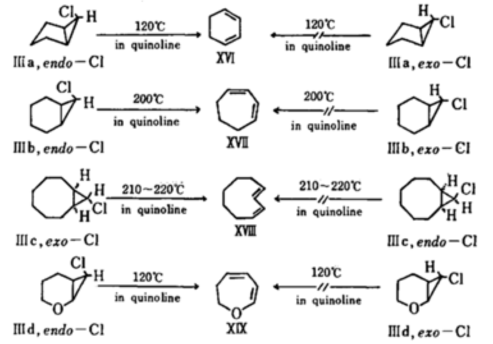


The above arguments predict that if the transition state of type XIII is more stable than that of type XIV, the ring expansion of the *exo*-chloro isomer of *gem*-chlorofluorocyclopropanes must occur faster than that of the *endo*-chloro isomer. This was proved to be the case in the ring expansion of 9-chloro-9-fluorobicyclo[6.1.0]nonane (IIc); the treatment of an isomeric mixture of IIc with quinoline at 215—225°C resulted in the formation of monofluorocyclononadiene (XV)[24] with the *endo*-chloro isomer recovered. In view of the well-known higher stability of *trans*- than *cis*-cyclononene, and probably of *trans*- than *cis*-2-cyclononenyl cation, this result is by no means "anomalous." Similar apparent anomalies have been reported in the acetolysis of bicyclo[5.1.0]octyl and -[6.1.0]nonyl tosylates[26] as well as in the ring expansion of 9-bromobicyclo[6.1.0]nonane by aqueous chromous sulfate.[27]



IIc, *exo*-Cl XV IIc, *endo*-Cl

Ring Expansion of n-Halobicyclo[$n-3.1.0$]-alkanes (n=6, 7, and 9) and Their 2-Oxa Analogues (n=7) in Quinoline. As might be expected from the above discussion, the ring expansion of 6-chlorobicyclo[3.1.0]hexane (IIIa), 7-chlorobicyclo[4.1.0]heptane (IIIb), 9-chlorobicyclo[6.1.0]nonane (IIIc) and 7-chloro-2-oxabicyclo[4.1.0]heptane (IIId) also occurred with distinct stereospecificity; it was only the *endo*-chloro isomers of IIIa, IIIb, and IIId, or the *exo*-chloro isomer of IIIc that underwent the ring expansion when treated with quinoline at 120—220°C.



The more facile conversion of the *endo*-chloro, compared with the *exo*-chloro, isomer of IIId to 2,3-dihydroöxepin, does not agree with the experimental results reported by Schweizer and Parham,[8] who prepared an isomeric mixture of IIId by the addition of chlorocarbene, generated by the method of Closs and Closs,[28] to 2,3-dihydro-4*H*-pyran. They stated that the *exo*-chloro isomer of IIId decomposed more easily than the *endo*-chloro isomer, and attributed the difference in reactivity to an anchimeric assistance exerted by the *trans*-oxygen atom during the loss of the chlorine. Their structural assignment for the isomers of IIId, however, is tentative and lacks decisive evidence: it was based only on the idea that the sterically less hindered *exo*-chloro isomer must be formed in greater predominance than the more hindered *endo*-chloro isomer. In view of the findings by Closs[29] that chlorocarbene reacts with cyclohexene to yield more *endo*- than *exo*-chloronorcarane and with unsymmetrical olefins

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[25] C. H. DePuy, L. G. Schnack and J. W. Hausser, *J. Am. Chem. Soc.*, **88**, 3343 (1966).

[26] a) P. von R. Schleyer, G. W. Van Dine, U, Schöllkopf and J. Paust, *ibid.*, **88**, 2868 (1966). b) U. Schöllkopf, K. Fellenberger, M. Patsch, P. von R. Schleyer, T. Su and G. W. Van Dine, *Tetrahedron Letters*, **1967**, 3639.

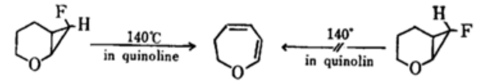
[27] H. Nozaki, T. Aratani and R. Noyori, *Tetrahedron*, **23**, 3645 (1967).

[28] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959).

[29] G. L. Closs, R. A. Moss and J. J. Coyle, *ibid.*, **84**, 4985 (1962).

to yield more *syn*-than *anti*-isomers, it is not surprising that the more hindered *endo*-chloro isomer is formed in greater predominance when it reacts with 2,3-dihydro-4H-pyran.

Both the *endo*-fluoro and the *exo*-fluoro isomers of 6-fluorobicyclo[3.1.0]hexane (IVa), 7-fluorobicyclo-[4.1.0]heptane (IVb), and 9-fluorobicyclo[6.1.0]-nonane (IVc) were quite stable under conditions similar to, or severer than, those used for the ring expansion of their chlorofluoro analogues. This is in good agreement with the observed lack of reactivity of the *exo*-chloro isomers of IIa, IIb, and IId or of the *endo*-chloro isomer of IIc, which evidently indicates the stability of the C–F bond, as compared with the C–Cl bond, in the ring expansion of halo- or dihalocyclopropanes.



IVd, *endo*-F XIX IVd, *exo*-F

The *endo*-fluoro isomer of 7-fluoro-2-oxabicyclo-[4.1.0]heptane (IVd), however, was converted to 2,3-dihydroöxepin (XIX) when heated at 140°C for 5 hr with an excess of quinoline. The enhanced reactivity of the *endo*-fluoro isomer of IVd, relative to that of IVa, IVb, and IVc, may be accounted for by the resonance effect of oxygen to stabilize the transition state of type XIV. The *exo*-fluoro isomer of IVd was recovered unchanged under similar conditions.

Experimental

General. The infrared spectra were obtained with a Shimadzu IR 27B Spectrophotometer. The UV spectra were measured with a Beckmann DB Spectrophotometer. The proton NMR spectra were obtained with a Varian Associates A-60, H-100, or a JEOL JNM C-60H Spectrometer in duteriochloroform or carbon tetrachloride with TMS as internal reference. Chemical shift data are given in δ values. The fluorine NMR spectra were obtained with a Hitachi High-Resolution NMR Spectrometer H-60 or a JEOL JNM C-60 (at 56.4 MHz) in carbon tetrachloride with trifluoroacetic acid as external reference. Gas chromotography (glpc) was performed on a Shimadzu GC-2C or a Yanagimoto 5DH Chromatograph. The analytical columns were 3 m×3 mm of 7.5% apiezon grease L, 10% tricresyl phosphate, 5% silicone grease, or 10% polyethylene glycol 6000 on 60/80 mesh or 80/100 mesh celite 550 or chromosorb W; the preparative columns were 2 m×10 mm of either 30% apiezon grease L or 30% tricresyl phosphate on 60/80 mesh celite 550. The percentage composition of isomers was estimated from peak areas of glpc or NMR signals.

General Procedure for Preparation of *n*,*n*-Dichlorobicyclo[*n*−3.1.0]alkanes (*n*=6, 7, and 9) and Their 2-Oxa Analogues (*n*=7). In a 200-m*l* five-necked flask fitted with a reflux condenser, a stirrer, a thermometer, a dropping funnel and an inlet tube for nitrogen, was placed a mixture of 4.9 g (0.2 mol) of sodium hydride (as a 50% dispersion in mineral oil), 0.2 mol of the corresponding olefin, and 20 m*l* of anhydrous ether. To the mixture was added under nitrogen, 35.5 g (0.2 mol) of methyl trichloroacetate and then 7 g (0.22 mol) of methanol, both dropwise at *ca.* 0°C. The addition of methanol required about 2 hr. After the reaction mixture was let to stand overnight, a small amount of methanol, and subsequently 70 m*l* of water, were gradually added. The organic layer was separated, the aqueous layer was extracted with ether, and the combined organic layer was washed with aqueous sodium hydroxide and with water. After being dried over anhydrous calcium chloride, it was distilled in vacuum to give *gem*-dichlorocyclopropanes. In the distillation of Ia, care had to be taken in order to avoid its isomerization to V. The yields and the properties of the products are given in Table 1.

General Procedure for Preparation of *n*-Chloro-*n*-fluorobicyclo[*n*−3.1.0]alkanes (*n*=6,7, and 9) and Their 2-Oxa Analogues (*n*=7). The procedure was essentially the same as above, except that 32.2 g (0.2 mol) of methyl dichlorofluoroacetate was used instead of methyl trichloroacetate, and that methanol was added at *ca.* 25—35°C instead of *ca.* 0°C. The yields and the properties of the products are given in Table 1. The gas chromatograms of IIa and IIb thus prepared had two peaks, the ratio of the areas of which was taken to be equal to the ratio of the weights of the isomers. The isomer distribution of IIc and IId, which showed only a single peak in glpc under various conditions, was determined from the integrated areas of the fluorine NMR peaks.

General Procedure for Reduction of *n*,*n*-Dichloro- and *n*-Chloro-*n*-fluorobicyclo[*n*−3.1.0]alkanes (*n*=6,7, and 9) and Their 2-Oxa Analogues (*n*=7). A mixture of 0.1 mol of *n*,*n*-dichloro- or *n*-chloro-*n*-fluorobicyclo[*n*−3.1.0]alkane, 29.1 g (0.1 mol) of tri-*n*-butyltin hydride, and a small amount of azobisisobutyronitrile or di-*t*-butyl peroxide was heated, with stirring, at the temperature shown in Table 3 until an aliquot from the reaction mixture showed no IR absorption due to Sn–H stretching (near 1820 cm^{-1}). The product was isolated by distillation, and the isomer ratio was determined by glpc.

Ring Expansion of 6,6-Dichlorobicyclo[3.1.0] hexane (Ia). In a flask fitted with a reflux condenser and a thermometer, a mixture of 7.6 g (0.05 mol) of Ia and 18 g (0.15 mol) of quinoline was heated at 120°C for 5 hr. After distillation (85—95°C/20 mmHg), the product was purified by preparative gas chromatography, and identified to be 2,3-dichlorocyclohexene by comparison of its refractive index and IR spectrum with those of an authentic sample;[22b)] n_D^{20} 1.5155, $\nu_{C=C}$ 1640 cm^{-1}.

Found: C, 47.80; H, 5.52%. Calcd for $C_6H_8Cl_2$: C, 47.71; H, 5.34%.

Further heating of the above reaction mixture at 140°C for 5 hr gave 82% yield of 2-chloro-1,3-cyclohexadiene, bp 70°C/78 mmHg, n_D^{20} 1.5055, IR (cm^{-1}): 3045 (m), 2940 (s), 2820 (s), 1632 (s), 1590 (w), 1440 (m), 1430 (s), 1390 (s), 1028 (s), 945 (s), 805 (s), and 720 (s).

Found: C, 62.85; H, 6.33%. Calcd for C_6H_7Cl: C, 62.90; H, 6.16%.

Ring Expansion of 7,7-Dichlorobicyclo[4.1.0] heptane (Ib). A mixture of 30 g (0.18 mol) of Ib and 77.4 g (0.6 mol) of quinoline was heated at 200°C in a

200-m*l* flask fitted with a reflux condenser and a thermometer. After 4 hr, the reflux of the reaction mixture became vigorous and the temperature in the flask lowered to below 180°C. At this temperature the mixture was heated for an additional 6 hr. Distillation of the reaction mixture gave 16 g (61% yield) of 1,3,5-cycloheptatriene which was identified by comparing its IR, UV, and NMR spectra with those of an authentic sample;[21] bp 108—110°C, n_D^{20} 1.5235, λ_{max}^{EtOH} 261 mμ (ε 3700).

Found: C, 91.46; H, 8.54%. Calcd for C_7H_8: C, 91.25; H, 8.75%.

Ib was heated at 200°C for 26 hr without quinoline. Although the generation of hydrogen chloride was noted, the glpc analysis of the reaction mixture showed no definite products. The starting material was almost completely recovered by distillation.

Ring Expansion of 7,7-Dichloro-2-oxabicyclo-[4.1.0]heptane (Id). A mixture of 8.3 g (0.05 mol) of Id and 50 g (0.39 mol) of quinoline was heated at 120°C for 6 hr. Distillation of the reaction mixture gave 5.2 g (80% yield) of 2,3-dihydro-6-chlorooöxepin, bp 85—90°C/14 mmHg, n_D^{21} 1.5183.

Found: C, 55.31; H, 5.32%. Calcd for C_6H_7ClO: C, 55.19; H, 5.40%.

Ring Expansion of 6-Chloro-6-fluorobicyclo-[3.1.0]hexane (IIa). A mixture of 6.7 g (0.05 mol) of IIa (isomeric mixture) and 18 g (0.15 mol) of quinoline was heated at 110°C for 5 hr. Distillation of the reaction mixture afforded 70% yield of 2-fluoro-3-chlorocyclohexene (X) and the unchanged *exo*-chloro isomer, which were separated by preparative gas chromatography. IR (cm^{-1}) of X: 2940 (s), 1702 (s), 1380(s), 1150 (s), 975 (s), 885 (s), and 705 (s).

The above reaction mixture was heated at 140°C for an additional 5 hr. 2-Fluoro-1,3-cyclohexadiene was obtained in 49% yield; n_D^{20} 1.4520, IR (cm^{-1}): 3020 (w), 2970 (s), 2850 (m), 1670 (s), 1595 (w), 1410 (s), 1165 (s), 815 (m), 795 (m), and 730 (m).

Found: C, 73.61; H, 7.22%. Calcd for C_6H_7F: C, 73.45, H, 7.19%. The *exo*-chloro isomer was completely recovered.

Ring Expansion of 7-Chloro-7-fluorobicyclo-[4.1.0]heptane (IIb). A mixture of 30 g (0.2 mol) of IIb (isomeric mixture) and 90 g (0.7 mol) of quinoline was heated at 200°C for 10 hr. Distillation of the reaction mixture afforded 5.2 g (50% yield based on the *endo*-chloro isomer) of 1,3,5-cycloheptatriene and 12.5 g of the unchanged *exo*-chloro isomer.

A mixture of IIb (isomeric mixture), ethylbenzene (as internal reference), and quinoline was heated at 200°C. Glpc analysis indicated that the *endo*-chloro isomer was lost completely after 10 hr, while the *exo*-chloro isomer remained unchanged.

Ring Expansion of 7-Chloro-7-fluoro-2-oxabicyclo[4.1.0]heptane (IId). A mixture of 10 g (0.065 mol) of IId (isomeric mixture) and 42 g (0.33 mol) of quinoline was heated at 120°C for 3 hr. Distillation of the reaction mixture gave two fractions, (a) bp 51—57°C/45 mmHg, 3.5 g, and (b) bp 70—80°C/25—30 mmHg, 3.5g. Redistillation of fraction (a) gave 77% yield(based on the *endo*-chloro isomer)of pure 2,3-dihydro-6-fluorooöxepin; bp 58—60°C/65 mmHg, n_D^{21} 1.4706, IR (cm^{-1}): 3024 (m), 2995 (m), 2945 (m), 2913 (m), 1670 (m), 1628 (m), 1420 (s), 1290 (s), 1238 (s), 1126 (vs), 928 (s), and 740 (s).

Found: C, 63.30; H, 6.25%. Calcd for C_6H_7FO: C, 63.15; H, 6.18%. Fraction (b) was the unchanged *exo*-chloro isomer.

Ring Expansion of 6-Chlorobicyclo[3.1.0]hexane (IIIa). A mixture of 5.8 g (0.05 mol) of IIIa (isomeric mixture) and 18 g (0.15 mol) of quinoline was heated at 120°C for 4 hr. Distillation of the reaction mixture gave 80% (based on the *endo*-chloro isomer) of 1,3-cyclohexadiene; bp 78—80°C, n_D^{20} 1.4756, and the unchanged *exo*-chloro isomer which was recovered unchanged even after being heated at 140°C for an additional 10 hr.

Found: C, 89.80; H, 10.20%. Calcd for C_6H_8: C, 89.94; H, 10.06%.

Ring Expansion of 7-Chlorobicyclo[4.1.0]heptane (IIIb). A mixture of 14 g (0.11 mol) of IIIb (isomeric mixture) and 45 g (0.35 mol) of quinoline was heated at 140°C for 5 hr. Glpc analysis of the reaction mixture showed that no reaction had occurred. The mixture was then heated at 200°C for 10 hr. Distillation of the reaction mixture gave 6.2 g (80% yield based on the *endo*-chloro isomer) of 1,3-cycloheptadiene; bp 118—120°C, n_D^{20} 1.4970, λ_{max}^{EtOH} 246 mμ (ε 7500), and 3.0 g of the unchanged *exo*-chloro isomer.

Found: C, 89.15; H, 10.84%. Calcd for C_7H_{10}: C, 89.29; H, 10.71%.

Heating of IIIb (isomeric mixture) without quinoline at 165°C for 19 hr gave a small amount of black, tarry material, but no diene product.

Ring Expansion of 7-Chloro-2-oxabicyclo[4.1.0] heptane (IIId). A mixture of 8.5 g (0.064 mol) of IIId (isomeric mixture) and 20 g (0.16 mol) of quinoline was heated at 120°C for 3 hr. Distillation of the reaction mixture gave 2.0 g (70% yield based on the *endo*-chloro isomer) of 2,3-dihyroöxepin; bp 56°C/10 mmHg, n_D^{22} 1.4958, and 4.2 g of the unchanged *exo*-chloro isomer which was recovered unchanged even after heated in quinoline at 120°C for 10 hr.

Found: C 74.78; H 8.30%. Calcd for C_6H_8O: C, 74.97; H, 8.39%.

Ring Expansion of 6-Fluorobicyclo[3.1.0]hexane (IVa) and 7-fluorobicyclo[4.1.0]heptane (IVb). A mixture of IVa or IVb (isomeric mixture), ethylbenzene (internal reference), and quinoline was heated at 200°C for 10 hr in a sealed tube. Glpc analysis of the reaction mixture proved that neither of the isomers had decomposed under these conditions.

Ring Expansion of 7-Fluoro-2-oxabicyclo[4.1.0] heptane (IVd). An isomeric mixture of IVd did not show any appreciable change when heated in quinoline at 120°C for 10 hr, but prolonged heating at 140°C for an additional 5 hr resulted in the decomposition of the *endo*-fluoro isomer to yield 2,3-dihyroöxepin (in a low yield), with recovery of the *exo*-fluoro isomer.

Ring Expansion of 9,9-Dichloro- (Ic), 9-Chloro-9-fluoro- (IIc), 9-Chloro- (IIIc), and 9-Fluorobicyclo [6.1.0]nonane (IVc). A mixture of Ic, IIc, IIIc, or IVc and quinoline was heated at 200—220°C for 10 hr. After distillation of the reaction mixture, the products were purified by preparative gas chromatography. Chlorocyclononadiene (VIII); bp 94°C/17 mmHg, n_D^{22} 1.5130, IR (cm^{-1}): 3015 (m), 2940 (s), 2860 (s), 1625 (s), 1590 (w), 1460 (s), 1040 (s), 950 (s), and 785 (s), NMR: δ 1.3—2.5 (m) (10H) and δ 5.5—6.0 (m) (3H).

Found: C, 69.12; H, 8.28%. Calcd for $C_9H_{13}Cl$: C, 69.00; H, 8.37%. Fluorocyclononadiene (XV); bp

98°C/70 mmHg, n_D^{21} 1.4783, IR (cm^{-1}): 3015 (m), 2940 (s), 2860 (s), 1690 (s), 1640 (w), 1460 (m), 1450 (m), 1120 (s), 1115 (m), 840 (m), and 750 (m). NMR: δ 1.2—2.6 (m) (10H) and δ 4.8—6.0 (m) (3H).

Found: C, 77.16; H, 9.52%. Calcd for $C_9H_{13}F$: C, 77.10; 9.35%. Cyclononadiene (XVIII); bp 105°C/83 mmHg, n_D^{21} 1.4940, IR (cm^{-1}): 3020 (s), 2940 (s), 2860 (s), 1630 (w), 1458 (s), 770 (s), and 734 (s), NMR: δ 1.2—2.4 (m) (10H) and δ 5.1—5.9 (m) (4H).

Found: C, 88.23; H, 11.77%. Calcd for C_9H_{14}: C, 88.45; H, 11.55%.

The *endo*-chloro isomer of IIc or IIIc and both isomers of IVc remained unchanged after being heated at 220°C for an additional 10 hr.