The Reaction of *endo*- and *exo*-2-Norborneol with Thionyl Chloride

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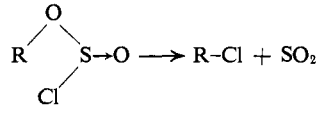
Abstract: The reaction of *endo*-2-norborneol (**1**) with thionyl chloride employing various solvents and conditions led to the formation of *endo*- (**3**) and *exo*-2-chloronorbornane (**4**) as well as *endo*-2-dinorbornyl sulfite (**5**), *endo*-2-norbornyl chlorosulfite (**7**), nortricyclene (**10**), and 4-chlorobutyl-*exo*-norbornyl ether (**12**). Similarly, *exo*-2-norborneol (**2**) yielded **3, 4, 10, 12,** as well as *exo*-2-dinorbornyl sulfite (**6**) and norbornene (**9**), although the very reactive intermediate *exo*-2-norbornyl chlorosulfite (**8**) could not be isolated. Treatment of *endo*-2-norborneol-2,3,3-d_3 (**15**), *endo*-2-norbornyl chlorosulfite-2,3,3-d_3 (**19**), or *exo*-2-norborneol-2,3,3-d_3 (**16**) led to skeletally transformed chlorides *via* a 6,2-hydride shift and a Wagner–Meerwein rearrangement, the ratios being about 80:20, 50:50, and 40:60, respectively. The mechanistic features of these results are discussed.

In the course of a study involving isotopically labeled derivatives of bicyclo[2.2.1]heptane, it became necessary to convert *endo*-2-norborneol-2,3,3-d_3 (**15**) to *exo*-2-chloronorbornane-2,3,3-d_3 (**18**) without proceeding through a carbonium ion which would lead to skeletal rearrangement.[2] A very promising approach to this transformation appeared to be through the use of thionyl chloride in the presence of pyridine, since optically active 2-octanol is known to afford the corresponding alkyl chloride in pyridine with a higher degree of inversion than that obtained with thionyl chloride alone.[3] In addition, other secondary alkyl alcohols in the presence of thionyl chloride and pyridine form only a single product as determined by vpc analysis.[4] Reports[5-10] of the conversion of hydroxyl groups to chlorides employing thionyl chloride in the bicyclo[2.2.1]heptane series in certain instances[5-8] can be explained on the basis of formation of either a classical or nonclassical carbonium ion.

The decomposition of alkyl chlorosulfites (chlorosulfinates) is one of the classic examples of the SNi reaction.



$$R\text{–}O\text{–}S(=O)\text{–}Cl \longrightarrow R\text{–}Cl + SO_2$$

However, the originally proposed mechanism[11] has required extensive modification since the decomposition of secondary chlorosulfites proceeds *via* a solvated carbonium ion with nearly complete retention of configuration in dioxane and inversion in toluene.[12-14] Decomposition of an optically active primary chlorosulfite in dioxane yielded a product which had partially racemized, presumably through a primary carbonium chlorosulfite ion-pair intermediate.[15]

Other analogous systems considered to afford products *via* the SNi reaction include alkyl chloroformates,[16,17] aralkyl thiocarbonates,[18] and alkyl chloroglyoxalates.[19] While alkyl chloroformates and aralkyl thiocarbonates undergo decomposition involving the formation of a carbonium ion, in the case of alkyl chloroglyoxalates the experimental results[19] are conflicting as to whether a carbonium ion is formed.

Results

endo-**2-Norborneol.** Treatment of *endo*-2-norborneol (**1**) with thionyl chloride employing various conditions and solvents (Table I) afforded chloronorbornane in which the chlorine was nearly exclusively *exo* (**4**) rather than *endo* (**3**), as indicated by vpc analyses. The use of pyridine as a solvent or in catalytic amounts had a profound effect on the course of the reaction because only chloronorbornane was formed (runs 1, 3, and 11). When pyridine in catalytic amounts was not added, numerous other products (Figure 1) were obtained in various solvents. In ether, under reflux conditions (run 2), the major product was nortricyclene (**10**); however, under very mild conditions in ether (runs 4–6) it was possible to convert *endo*-2-dinorbornyl sulfite (**5**) into *endo*-2-norbornyl chlorosulfite (**7**). In tetrahydrofuran (runs 7 and 8) an additional product, 4-chlorobutyl-*exo*-2-norbornyl ether (**12**),[20] was isolated, while in dioxane, a solvent base not susceptible to ring opening, no side products were observed.

exo-**2-Norborneol.** When *exo*-2-norborneol (**2**) was also treated with thionyl chloride (Figure 1) by employing similar conditions and solvents (Table II) again *exo*-2-chloronorbornane (**4**) rather than the *endo* isomer (**3**) was formed. In the presence of pyridine

(1) (a) This paper is taken in part from the Ph.D. Dissertation of F. M. S., University of Iowa, 1966. (b) National Aeronautics and Space Administration Trainee, 1964–1966.
(2) J. A. Berson in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 111.
(3) W. Gerrard and H. R. Hudson, *J. Chem. Soc.*, 1059 (1963).
(4) J. Cason and J. S. Correia, *J. Org. Chem.*, **26**, 3645 (1961).
(5) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).
(6) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, 72, 3329 (1950).
(7) S. Winstein, *Experientia Suppl.*, 2, 137 (1955).
(8) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 378 (1965).
(9) S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).
(10) R. S. Neale and E. B. Whipple, *ibid.*, **86**, 3130 (1964).
(11) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).
(12) E. S. Lewis and C. E. Boozer, *J. Am. Chem. Soc.*, 74, 308 (1952).
(13) C. E. Boozer and E. S. Lewis, *ibid.*, **75**, 3182 (1953).
(14) C. E. Boozer and E. S. Lewis, *ibid.*, **76**, 794 (1954).
(15) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 379 (1957).
(16) K. B. Wiberg and T. N. Shryne, *ibid.*, 77, 2774 (1955).
(17) K. L. Olivier and W. G. Young, *ibid.*, **81**, 5811 (1959).
(18) J. L. Kice, R. A. Bartsch, M. A. Dankleff, and S. L. Schwartz, *ibid.*, **87**, 1734 (1965).
(19) S. J. Rhoads and R. E. Michel, *ibid.*, **85**, 585 (1963).
(20) Since the infrared and nmr spectra of product 12 was identical when prepared from 1 or 2, the *exo* configuration was assigned.

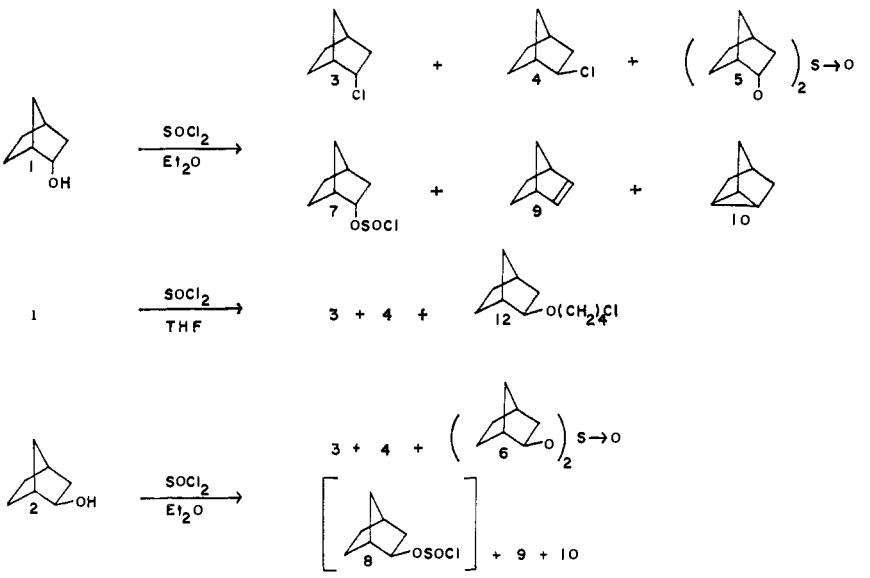


Figure 1.

as solvent or catalyst (runs 12 and 14), only chloronorbornane was formed while in the absence of pyridine numerous side products were formed. In ether, under reflux conditions (run **13**), the major product was again nortricyclene (**10**) while under milder conditions (runs 15–17) *exo*-2-dinorbornyl sulfite (**6**) was isolated. No *exo*-2-norbornyl chlorosulfite (**8**) could be isolated. In addition the reaction between **6** and thionyl chloride, a method known to yield other very reactive chlorosulfites,[21,22] afforded only the *exo*-chloride (**4**) (Table III). This is undoubtedly due to the propensity of

Table I. Reactions of *endo*-2-Norborneol (**1**) with Thionyl Chloride

Run no.	Reactants $SOCl_2$, **1**, moles	Reaction conditions: Solvent, ml	Time, hr	Temp, °C	Products, %: **4**	**5**	**7**	**10**	**12**
1	0.15, 0.10	Pyridine, 8	1	100[a]	65				
			24	25					
2	0.02, 0.02	Ether, 10	2	Reflux	9	...	...	20	
3	0.02, 0.02	Ether, 10[b]	2	Reflux	58				
4	0.15, 0.10	Ether, 100	2	−20	11	32	0	16[c]	
5	0.15, 0.10	Ether, 100	2	−20	32	0	19	5	
			3	25					
6	0.15, 0.10	Ether, 100	2	−20	15	0	38	0	
			24	25					
7	0.04, 0.04	THF, 15	2	Reflux	19	...	...	...	42
8	0.06, 0.04	THF, 20	2	Reflux	49	...	...	...	15
9	0.06, 0.04	Dioxane, 20	2	Reflux	65				
10	0.28, 0.20	Benzene, 50	0.5	Reflux	18	30			
11	0.14, 0.10	Benzene, 25[b]	0.5	Reflux	36				

[a] When two times and temperatures are listed, the reaction was run at the first temperature followed by the second for the corresponding time. [b] Four drops of pyridine were added. [c] Vpc ratio of nortricyclene (**10**) to norbornene (**9**) was 97:3.

Table II. Reactions of *exo*-2-Norborneol (**2**) with Thionyl Chloride

Run no.	Reactants $SOCl_2$, **2**, moles	Reaction conditions: Solvent, ml	Time, hr	Temp, °C	Products, %: **4**	**6**	**9**	**10**	**12**
12	0.023, 0.015	Pyridine, 1.6	1	100[a]	39				
			24	25					
13	0.02, 0.02	Ether, 10	2	Reflux	23	...	5	28	
14	0.02, 0.02	Ether, 10[b]	2	Reflux	45				
15	0.15, 0.10	Ether, 100	2	−20	27	60	...	1	
16	0.15, 0.10	Ether, 100	2	−20	55	26	...	5	
			24	0					
17	0.15, 0.10	Ether, 100	2	−20	69	0	...	4	
			48	0					
18	0.04, 0.04	THF, 15	2	Reflux	57	...	...	...	20
19	0.06, 0.04	THF, 20	2	Reflux	62	...	...	...	13
20	0.06, 0.04	Dioxane, 20	2	Reflux	51				

[a] See Table I, footnote *a*. [b] See Table I, footnote *b*.

(21) W. Gerrard, A. Nechvatal, and B. M. Wilson, *J. Chem. Soc.*, 2088 (1950).

(22) P. D. Bartlett and H. F. Herbrandson, *J. Am. Chem. Soc.*, **74**, 5971 (1952).

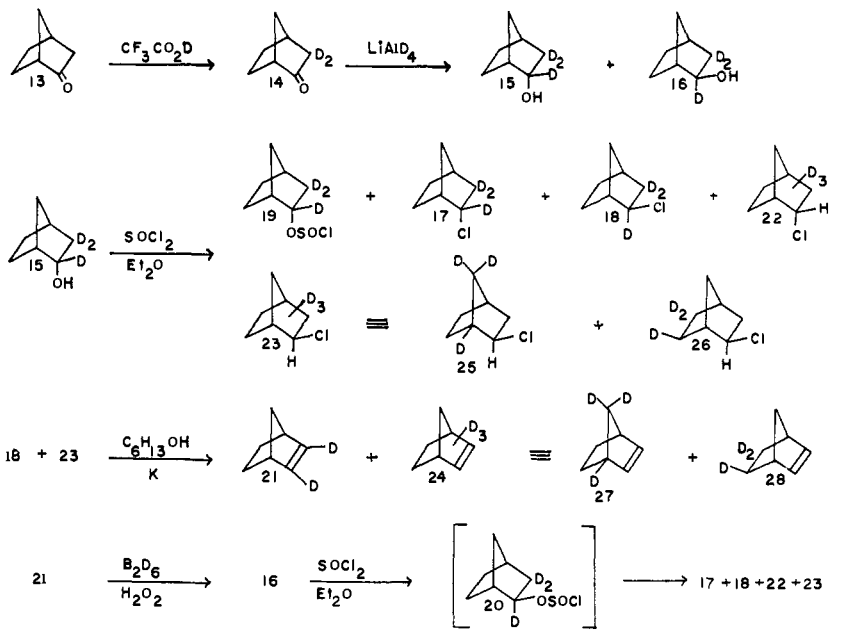


Figure 2.

the *exo* isomer in the bicyclo[2.2.1]heptane system to undergo enhanced solvolysis.[23] In tetrahydrofuran (runs 18 and 19) the ether **12** was formed but in smaller amounts than in the reaction with **1**. Again only in dioxane (run 20) were no side products obtained.

Table III. Reactions of *endo*- (**5**) and *exo*-2-Dinorbornyl Sulfite (**6**) (Ether Solvent)

Reactant, disulfite	Reaction conditions Time, hr	Temp, °C	—Composition ratio[a]— 1	2	4
5	0.5	25[b]	46		54[c]
5	0.5	25[b,d]	45		55[c]
	24	25			
6	0.5	25		42	58[e]
6	0.5	25[b,d]		44	56[e]
	24	25			
6[f]	2	−20			81[g]
	48	0			

[a] Retention times of 42 min for **3**, 45 min for **4**, 88 min for **1**, and 94 min for **2** were observed using a 5% Zonyl E-7 (40 ft × 0.25 in.) column at 100° with a helium flow of 86 ml/min. [b] Dry hydrogen chloride was slowly bubbled through the solution for 0.5 hr. [c] The ratio of **3** to **4** was 2.5:97.5. [d] See Table I, footnote *b*. [e] Vpc analysis failed to detect the presence of **3**. [f] An equimolar amount of thionyl chloride was added. [g] Per cent yield of **4**.

Labeled *endo*-2-Norborneol. The preferred mode of attack in the bicyclo[2.2.1]heptane series is from the least hindered *exo* side,[24] and thus a skeletal rearrangement *via* a carbonium ion can proceed undetected unless the starting material is labeled. Consequently, *endo*-2-norborneol-2,3,3-d_3 (**15**) was prepared (Figure 2) by deuterium exchange with norcamphor (**13**) followed by the reduction of 3,3-dideuterionorcamphor (**14**) with lithium aluminum deuteride.[25] The number of atoms of deuterium per molecule for **14** and **15** was 1.966 and 2.886, respectively, corresponding to 98.3 and 96.2% purity as determined by quantitative nmr analysis.

When the *endo* epimer (**15**) was treated with thionyl chloride under the reaction conditions shown in Table IV, *endo*- (**17**) and *exo*-2-chloronorbornane-2,3,3-d_3 (**18**) as well as first rearranged products *endo*- (**22**) and *exo*-chloride (**23**) were formed in all cases. However, in the presence of pyridine as a solvent or a catalyst, only partial skeletal rearrangement, 24–36%, was observed.

Dehydrochlorination of the mixture of isomerically deuterated chloronorbornanes (Figure 2) employing potassium 3-methyl-3-pentoxide in 3-methyl-3-pentanol[26] yielded only the isomerically deuterated norbornenes (**21**, **27**, and **28**); no nortricyclene was present. A mass spectral analysis of the deuterated chlorides (**18**, **25**, and **26**) showed 95.3% d_3, 4.6% d_2, and 0.1% d_4. The olefinic composition was 1% d_4, 34.2% d_3 (**27** and **28**), 61.8% d_2 (**21**), and 3.0% d_1. The nmr analysis of this reaction showed that the skeletally rearranged chlorides **25** and **26** amounted to 38% and that the ratio of **25** to **26** was 19:81, respectively, while the skeletally rearranged olefins **27** and **28** amounted to 35%.

In order to exclude the possibility that rearrangement might occur during the initial formation of the chlorosulfite ester, *endo*-2-norbornyl chlorosulfite-2,3,3-d_3 (**19**) was prepared from the *endo* epimer (**15**). The nmr spectrum of **19** revealed that no rearrangement and complete retention of configuration had occurred since there was no evidence of a proton on the carbon bearing the chlorosulfite group. Direct pyrolysis or decomposition of **19** in solvent (Table IV) still led to some rearranged chloride **23**. The chloronorbornanes formed from **19** were >99% *exo* as shown by vpc analyses.

Labeled *exo*-2-Norborneol. The hydroboration[27] of 2,3-dideuterionorbornene (**21**) led to the formation of *exo*-2-norborneol-2,3,3-d_3 (**16**). The number of atoms

(23) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(24) L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 82, 2341 (1960).

(25) The reduction also gives 9% of the *exo* isomer **16**, but its presence does not interfere with a detailed interpretation of the reactions of the *endo*-alcohol: C. F. Wilcox, M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, 28, 1079 (1963).

(26) H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, 86, 2601 (1964).

(27) G. Zweifel and H. C. Brown, *Org. Reactions*, 13, 30 (1963).

Table IV. Reactions of *endo*- (**15**) and *exo*-2-Norborneol-2,3,3-d_3 (**16**) and *endo*-2-Norbornyl Chlorosulfite-2,3,3-d_3 (**19**) with Thionyl Chloride

Reactants		Reaction conditions			Products,	Composition ratio[a]			
Alcohol	$SOCl_2$, ROH mole	Solvent, ml	Time, hr	Temp, °C	% 18 and 23	18	23	25	26
15	0.0075, 0.005	Ether,[b] 5	2	Reflux	57	76	24	6	18
15	0.11, 0.075	Pyridine, 6	1	100[c]	69	62	38	7	31
			24	25					
15	0.0075, 0.005	Dioxane, 5	2	Reflux	38	40	60	9	51
15	0.075, 0.05	Ether, 50	2	−20	13[d]	37	63	10	53
			24	25					
19	... ...	Ether,[b] ...	2	Reflux	52	84	16	9	7
19	... ...	Pyridine, ..	1	100	23	76	24	11	13
			24	25					
19	... ...	None	0.5	180	34	71	29	10	19
16	0.0068, 0.0045	Ether,[b] 5	2	Reflux	48	68	32	18	14
16	0.0068, 0.0045	Pyridine, 5	1	100	39	59	41	12	29
			24	25					
16	0.0068, 0.0045	Dioxane, 5	2	Reflux	46	53	47	20	27

[a] Deuterium contents in all cases were determined by integration of the appropriate signals of the nmr spectra, by assuming either a single 6,2-hydride shift (6,2-H) or a Wagner–Meerwin rearrangement (W–M) had taken place. An initial 6,2-H followed by several successive W–M and 6,2-H would increase the product analyzed as arising from a W–M rearrangement. Thus, the value is somewhat low for **26** and high for **25**. [b] See Table I, footnote *b*. [c] See Table I, footnote *a*. [d] In this case a 40% yield of **19** was also formed.

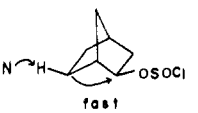
of deuterium per molecule for **21** and **16** was 1.848 and 2.73, respectively, corresponding to 92.4 and 91.0% purity. When **16** was subjected to reaction with thionyl chloride 32–47% rearrangement occurred (Table IV), *via* formation of the elusive *exo*-2-norbornyl chlorosulfite-2,3,3-d_3 (**20**), to yield products **18** and **23**.

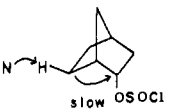
Discussion

The reactions of the norborneols with sulfonyl chloride are sensitive to reaction conditions, particularly with respect to solvent, in that a variety of products can be obtained. The first product of the reaction, the chlorosulfite ester, could be isolated only in the case of the reaction of the *endo* epimer. When the dinorbornyl sulfite esters were treated with dry hydrogen chloride, a reaction which affords chlorosulfite ester,[28,29] the *endo*-chlorosulfite (**7**) was obtained, but the *exo* isomer (**6**) affords only the *exo*-chloride (**4**). Inability to isolate the *exo*-chlorosulfite ester can be attributed to its extremely rapid solvolysis.[30]

In the decomposition of the intermediate chlorosulfite, the formation of olefins by a stereospecific *cis* elimination has been observed; carbenes and cyclopropanes have been eliminated as intermediates in the olefin formation.[31,32] Yet it is interesting to note that when **1** is treated with thionyl chloride, the elimination product is nortricyclene (**10**) rather than norbornene (**9**). Even in the reactions of the *exo*-alcohol (**2**) the elimination product is mainly nortricyclene (**10**) and not norbornene (**9**). It has been shown[33] recently that **9** and not **10** is the normal product for the E2 elimination in the norbornyl system and that **10** must result from an E1 reaction rather than an E2 process, since the percentage of elimination product increases as the dielectric constant increases. Other workers[34–36] have reported that **10** is the major product from dehydration of **2** using phosphorus pentoxide or the dehydration of **1** and **2** over alumina at elevated temperatures, but **10** is the only product resulting from a direct displacement on **2**. If the precursor of **10** is considered to be the classical norbornyl cation, it is difficult to rationalize the nearly exclusive formation of a cyclopropane ring on elimination since olefinic products in the bicyclo[2.2.1] series are generally formed from carbonium ions.[37,38] If in the case of **1** the protonated cyclopropane structure were

the cationic precursor of **10**, then the nearly exclusive formation of **10** would be understandable, while for the *exo*-chlorosulfite (**8**) another type of concerted elimination reaction could occur by a nucleophilic attack on the proton attached to C-6. However, in



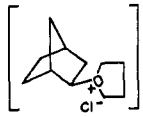


case of *endo*-chlorosulfite (**7**) a similar process is unfavorable as evidenced by consideration of electronic and stereochemical factors. The formation of mainly the *exo*-chloride (**4**) when **1** is treated with thionyl chloride must mean that the SNi reaction even without base occurs to a very limited extent.

In the reaction of the *endo*-alcohol (**1**), the formation of **12** can be envisioned as proceeding *via* an SN2 mechanism where the basic solvent tetrahydrofuran displaces the intermediate chlorosulfite (**7**). It is significant that the largest ratio of *endo*- (**3**) to *exo*-2-chloronorbornane (**4**), 4.7:95.3, arises from this reaction. The various products obtained from the decomposition of the oxonium ion are easily understood by

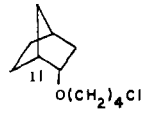
(28) W. Gerrard, *J. Chem. Soc.*, 85 (1944).
(29) W. E. Bissinger and F. E. Kung, *J. Am. Chem. Soc.*, **69**, 2158 (1947).
(30) S. Winstein and D. Trifan, *ibid.*, **74**, 1147 (1952).
(31) E. S. Lewis, W. C. Herndon, and D. C. Duffy, *ibid.*, **83**, 1959 (1961).
(32) E. S. Lewis and W. C. Herndon, *ibid.*, **83**, 1961 (1961).
(33) H. Kwart, T. Takeshita, and J. L. Nyce, *ibid.*, **86**, 2606 (1964).
(34) P. von R. Schleyer, *ibid.*, **80**, 1700 (1958).
(35) K. Watanabe, C. N. Pillai, and H. Pines, *ibid.*, **84**, 3934 (1962).
(36) J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, 30, 2639 (1965).
(37) A. Nickon and J. H. Hammons, *J. Am. Chem. Soc.*, **86**, 3322 (1964).
(38) R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964).

consideration of the alternateca rbon–oxygen bond-breaking reactions.



Loss of tetrahydrofuran leads to the formation of the norbornyl cation which would be attacked by chloride to yield exclusively *exo*-chloride (**4**). Scission of the ether bond with simultaneous attack of chloride ion at the two position on the tetrahydrofuran ring leads to the *exo*-alkoxide, **12**. Nucleophilic attack at the C-2 on the norbornyl skeleton from the *endo* or *exo* side involving displacement of the tetrahydrofuran by chloride would result in the formation of the *endo*- and *exo*-norbornyl chlorides **3** and **4**, respectively.

For the *exo* epimer (**2**), the reaction can proceed with prior ionization of **8** followed by addition of tetrahydrofuran to form **29**. Again the highest ratio of *endo*- to *exo*-chloride, 2.7:97.3, was found when using tetrahydrofuran as a solvent. Since only a few displacement reactions have been reported[37,39] for the *exo* isomer in the bicyclo[2.2.1]heptane system, it does not seem very likely that an *endo*-oxonium ion would be formed; the *endo*-alkoxide (**11**) was not isolated. Norbornyl ethers were



not isolated when diethyl ether was the solvent.

The reaction employing labeled norborneols provided additional information as to the mechanism of chlorosulfite decomposition. In general, when an alcohol is treated with thionyl chloride in the presence of pyridine as solvent or catalyst an SN2 reaction occurs.[40–42] Thus in the case of *endo*-2-norborneol-2,3,3-d_3 (**15**), it was expected that only *exo*-2-chlorononorbornane-2,3,3-d_3 (**18**) would be formed without skeletal rearrangement in the presence of pyridine. However, nmr analysis showed that 38% of the product had the chloride attached to a carbon bearing an *endo*-2-proton. Since *endo*-2-norbornyl chlorosulfite-2,3,3-d_3 (**19**) had been formed stereospecifically, rearrangement must have occurred during the decomposition of the chlorosulfite.

Three types of skeletal rearrangements have been well established for the 2-norbornyl cation: the Wagner–Meerwein rearrangement, the 6,2-hydride shift, and the 3,2-hydride shift. It has been observed that the 3,2-hydride shift is slower than the Wagner–Meerwein rearrangement and the 6,2-hydride shift by a minimum of $10^{8.8}$ times at $-120°$.[43]

Three general types of mechanisms can be written to account for this skeletal rearrangement (Figure 3). If the reaction proceeds by an SNi or SN2 path no skeletal rearrangement would have occurred (**17** and

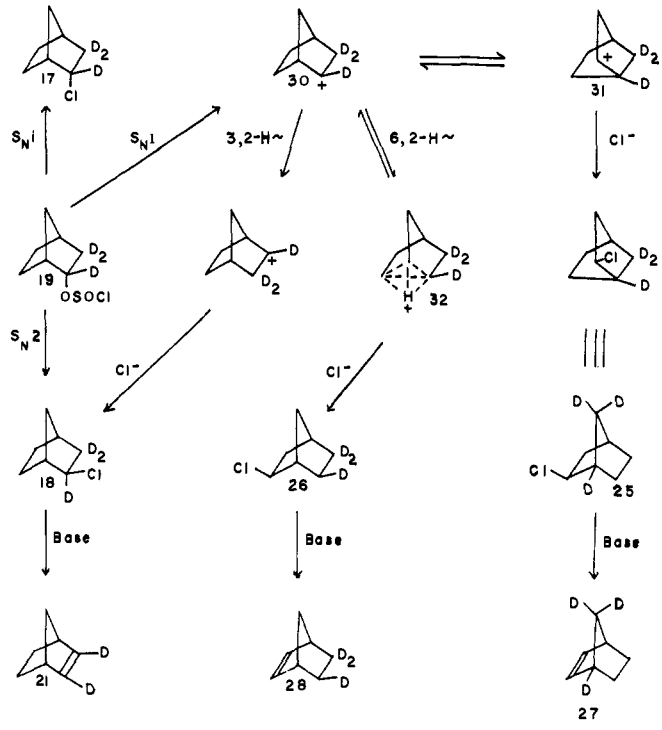
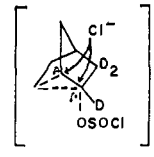


Figure 3.

18, respectively). If the reaction proceeds to give a norbornyl cation, **31**, not more than 50% rearrangement would be expected unless the secondary deuterium isotope effect favors ion **31** over **30**. When the reaction was run n ether, 63% rearrangement was observed, and in dioxane, 60% as detected by the appearance of a proton instead of a deuterium ion on the carbon bearing the chloride. It is significant that where dioxane has been employed as a solvent for optically active 2-pentanol in the presence of thionyl chloride, the alkyl chloride found had the same sign of rotation and an optical purity of 98.5%.[13] Ion **31** cannot alone account for all the rearrangement but **26**, resulting from a 6,2-hydride shift, could be responsible for this observation. The intermediate **32**, which is similar to that proposed for the solvolysis of *endo*-2,3-$^{14}C_2$-norbornyl brosylate to explain the ^{14}C activity in the C-5 and C-6 positions,[44] leads to **26**.

With catalytic amounts of pyridine in ether, only 24% of the product was the rearranged deuterated *exo*-chloride. This can be rationalized in one of two ways. As **19** begins to ionize, a more positive character resides on C-2 and an SN2 attack by chloride ion would favor C-2 rather than C-1. Very short carbonium ion



lifetimes have been found for some other bicyclic alcohols when treated with thionyl chloride.[8] Alternatively, part of the chlorosulfite could react by a chloride ion SN2 attack, while the remainder would decompose through an SN1 process.

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(40) F. D. Hughes, C. K. Ingold, and I. C. Whitfield, *Nature*, 147, 206 (1941).
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(42) E. S. Lewis and G. M. Coppinger, *J. Am. Chem. Soc.*, 76, 796 (1954).
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By integrating the appropriate signals of the nmr spectra, the deuterium content was determined so that it was possible to assess the relative amounts of a 6,2-hydride shift *vs.* a Wagner–Meerwein rearrangement (Table IV). Thus when the *endo*-alcohol (**15**) was treated in such a manner that the intermediate *endo*-chlorosulfite (**19**) was not isolatable, the relative amounts of 6,2-hydride shift *vs.* a Wagner–Meerwein rearrangement was found to be about 80:20.

Since the reaction of *endo*-2-norborneol-2,3,3-d_3 (**15**) with thionyl chloride employing various conditions always led to rearrangement, it was hoped that decomposition of *endo*-2-norbornyl chlorosulfite-2,3,3-d_3 (**19**) would proceed to product without undergoing a skeletal rearrangement. Decomposition of **19** (Table V) in the presence of catalytic amounts of pyridine gave the least amount of skeletal rearrangement, 16%, while pyrolysis of **19** led to 29% rearranged product. In these cases, the ratio of a 6,2-hydride shift *vs.* a Wagner–Meerwein rearrangement was about 50:50, indicating that complete equilibration between **31** and **32** occurs due to the initial solvolysis of the chlorosulfite **19** to **30**.

Table V. Decomposition of *endo*-2-Norbornyl Chlorosulfite (**7**)

Reaction conditions			Products, %
Solvent	Time, hr	Temp, °C	**4**
None	0.5	180	83
Ether[a]	2	Reflux	66
Pyridine	1	100[b]	62
	24	25	
Ether[c]	0	25	*d*
None[e]	24	25	*f*

[a] See Table I, footnote *b*. [b] See Table I, footnote *a*. [c] Mixture was immediately washed with 10% sodium carbonate. [d] Vpc ratio of **1** to **4** was 22:78. [e] Reaction occurred in an open vial. [f] Vpc ratio of **1** to **4** was 74:26.

When *exo*-2-norborneol-2,3,3-d_3 (**16**) was treated with thionyl chloride (Table IV) skeletal rearrangement occurred as expected. As in the case of the *endo*-chlorosulfite ester, if the reaction proceeds either by an SNi or SN2 path, no skeletal rearrangement would be expected. Skeletal rearrangements *via* a Wagner–Meerwein rearrangement and a 2,6-hydride shift occurred but to a less extent than with the *endo* isomer. The fact that the amount of skeletal rearrangement of the deuterated *endo*-alcohol (**15**) is greater than with the *exo* epimer (**16**) could mean that the chlorosulfite group leaves more slowly in the case of the *endo* epimer (**15**), providing there is a greater probability that the norbornyl cation will be long enough lived to rearrange before capture by chloride ion, exclusive of any SN2 reaction.

That rearrangement occurs quite extensively with **15** and **16** in the presence of thionyl chloride tends to indicate that this reaction lacks usefulness where stereospecificity is needed and the designation of this being an example of an SNi reaction is not correct when the formation of a carbonium ion is facile.

Experimental Section[45]

General Procedure for the Reaction of *endo*- (1) and *exo*-2-Norborneol (2) with Thionyl Chloride. To a cooled solution of alcohol in solvent was added thionyl chloride dropwise. The mixture was stirred at a specified temperature for a specified length of time. The mixture was either directly distilled, or poured into ice–water, extracted with ether, washed with 10% sodium carbonate, and dried. After evaporation of the ether, the residue was distilled.

General Procedure for the Decomposition of *endo*-2-Norbornyl Chlorosulfite (7). When no solvent was used, **7** was placed in a flask and warmed in an oil bath; or a solution of **7** in solvent was warmed for a length of time and then either directly distilled or poured into ice–water, extracted, and washed with 10% sodium carbonate. The organic layer was dried and, following evaporation of the solvent, the residue was distilled.

***endo*-2-Chloronorbornane (3).** The synthesis was carried out by hydrogenating the product obtained from the Diels–Alder reaction between cyclopentadiene and vinyl chloride.[46] Vpc analysis showed the ratio of *endo*- (**3**) to *exo*-chloride (**4**) to be 57.1:42.9, using a 5% Zonyl E-7 (40 ft × 0.25 in.) column at 75° and a helium flow of 100 ml/min.

***exo*-2-Chloronorbornane (4)**[47] was prepared by the addition of dry hydrogen chloride to norbornene.[48] The ratio of **3** to **4** was 1.5:98.5 as determined by vpc analysis. See Table VI for the conditions.

Table VI. Composition of *endo*- (**3**) and *exo*-2-Chloronorbornane (**4**) Obtained from the Reaction of *endo*-2-Norborneol (**1**) with Thionyl Chloride

	Composition ratio[a]	
Solvent	**3**	**4**
Ether[b]	0.2	99.8
Benzene	0.3	99.7
Pyridine	0.6	99.4
Dioxane	1.5	98.5
Ether	1.9	98.1
THF	4.7	95.3

[a] Retention times of 47 min for **3** and 50 min for **4** were observed using a 5% Zonyl E-7 (40 ft. × 0.25 in.) column at 95% and a helium flow of 86 ml/min. [b] See Table I, footnote *b*.

***exo*-2-Chloronorbornane (4).** To a solution of 11.2 g (0.1 mole) of *endo*-2-norborneol (**1**)[49,50] dissolved in 7.9 g (8.05 ml, 0.1 mole) of pyridine cooled in an ice bath was added 17.9 g (10.9 ml, 0.15 mole) of thionyl chloride dropwise. After 1 hr, the mixture was heated on a steam bath for 1 hr and was allowed to stand overnight. The solution was poured into 100 ml of ice–water and extracted with ether, and the organic layer was washed with 10% sodium carbonate, dried, and concentrated. There was obtained 8.8 g (65.2%) of product, bp 158–160° (lit.[51] bp 160–162°), n^{26}D 1.4818 (lit.[52] n^{25}D 1.4823).

***endo*-2-Dinorbornyl Sulfite (5).** To a solution of 11.2 g (0.1 mole) of *endo*-2-norborneol (**1**) in 50 ml of ether cooled to −30° was added 17.9 g (10.9 ml, 0.15 mole) of thionyl chloride in 50 ml of ether dropwise. During the addition the temperature was kept below −20°. After 2 hr in the cold bath, the solution was allowed to warm to 0°, and the solvent was removed under reduced pressure. The residue was distilled at 30 mm to afford 1.46 g (11.2%) of *exo*-2-chloronorbornane (**4**), bp 42–44° (10 mm), n^{20}D 1.4830, and 4.25 g (31.6%) of *endo*-2-dinorbornyl sulfite (**5**), bp 136–139° (1

(45) Gas chromatographic analyses were carried out with the F & M Model 500 instrument using either a 10% diisodecyl phthalate (8 ft × 0.25 in.) or a 5% Zonyl E-7 (40 ft × 0.25 in.) column. A Varian A-60 was used for nmr spectra with tetramethylsilane as the internal standard and carbon tetrachloride as the solvent. Infrared analyses were run on a Perkin-Elmer Infracord.

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(47) H. Kwart and R. K. Miller, *ibid.*, **78**, 5008 (1956).

(48) Obtained from the Aldrich Chemical Co.

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(50) S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956).

(51) G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).

(52) J. D. Roberts, L. Urbanek, and R. Armstrong, *J. Am. Chem. Soc.*, 71, 3049 (1949).

Table VII. Composition of *endo*- (**3**) and *exo*-2-Chloronorbornane (**4**) Obtained from the Reaction of *exo*-2-Norborneol (**2**) with Thionyl Chloride

Solvent	Composition ratio[a] 3	4
Ether	0.4	99.6
Ether[b]	0.6	99.4
Dioxane	0.7	99.3
Pyridine	1.5	98.5
THF	2.7	97.3

[a] See Table VI, footnote *a*. [b] See Table I, footnote *b*.

mm), n^{22}D 1.5085. The contents of the trap afforded 1.48 g (15.7%) of solid, bp 96–100° (lit.[34] bp 101.8–102°). Vpc analysis using a 10% diisodecyl phthalate (8 ft × 0.25 in.) column at 45° and a helium flow of 67 ml/min showed the ratio of nortricyclene (**10**)[53] to norbornene (**9**)[48] was 97:3. The retention times of **9** and **10** were 15 min and 19 min, respectively.

Anal. Calcd for $C_{14}H_{22}SO_3$: C, 62.19; H, 8.20. Found: C, 62.84; H, 8.18.

***exo*-2-Dinorbornyl Sulfite (6).** To a solution of 11.2 g (0.1 mole) of *exo*-2-norborneol (**2**)[27,54] in 50 ml of ether cooled to −30° was added 17.9 g (10.9 ml, 0.15 mole) of thionyl chloride in 50 ml of ether dropwise. During the addition the temperature was kept below −20°. After 2 hr in the cold bath, the solution was allowed to warm to 0°, and the solvent was removed under reduced pressure. The product was distilled at 0.5 μ to yield 8.14 g (60.2%) of *exo*-2-dinorbornyl sulfite (**6**), bp 105–107°, n^{20}D 1.5075. The presence of <1% nortricyclene (**10**) was found by vpc analysis of the trap; after distillation, 3.54 g (27.6%) of *exo*-2-chloronorbornane (**4**) was obtained.

Anal. Calcd for $C_{14}H_{22}SO_3$: C, 62.19; H, 8.20. Found: C, 62.41; H, 8.13.

***endo*-2-Norbornyl Chlorosulfite (7).** To a solution of 11.2 g (0.1 mole) of *endo*-2-norborneol (**1**) in 50 ml of ether cooled to −30° was added 17.9 g (10.9 ml, 0.15 mole) of thionyl chloride in 50 ml of ether dropwise. During the addition the temperature was kept below −20°. After 2 hr in the cold bath, the solution was kept at room temperature for 24 hr. The solvent was removed under reduced pressure and the product distilled at 7–9 μ to afford 7.33 g (37.6%) of *endo*-2-norbornyl chlorosulfite (**7**), bp 43–56°, n^{23}D 1.5108. The contents of the trap afforded 1.93 g (14.7%) of *exo*-2-chloronorbornane (**4**). Vpc analysis did not indicate the presence of any norbornene (**9**) or nortricyclene (**10**).

Anal. Calcd for $C_7H_{11}SO_2Cl$: C, 43.18; H, 5.70. Found: C, 44.12; H, 6.03.

4-Chlorobutyl *exo*-2-Norbornyl Ether (12). To a solution of 4.48 g (0.04 mole) of *endo*-2-norborneol (**1**) in 15 ml of tetrahydrofuran cooled in an ice bath was added 4.76 g (2.92 ml, 0.04 mole) of thionyl chloride dropwise. The mixture was heated at reflux temperature for 2 hr, and following the distillation of tetrahydrofuran and thionyl chloride, a distillation of the residue under reduced pressure afforded 0.99 g (19.1%) of *exo*-2-chloronorbornane (**4**), bp 54–56° (16 mm), n^{19}D 1.4828 (lit.[47] bp 54–55.5° (16 mm), n^{20}D 1.4842), and 3.44 g (42.4%) of 4-chlorobutyl *exo*-2-norbornyl ether (**12**), bp 114–116° (5 mm), n^{19}D 1.4790. The nmr spectra is in accord with the assignment. (See Tables VII and VIII.)

Anal. Calcd for $C_{11}H_{19}OCl$: C, 65.17; H, 9.45. Found: C, 65.29; H, 9.72.

Decomposition of *endo*-2-Norbornyl Chlorosulfite (7) in Ether. A. To a solution of 1.07 g (0.0055 mole) of **7** in 5 ml of ether cooled in an ice bath was added 4 drops of pyridine. The mixture was heated at reflux for 2 hr and, following a distillation of ether, there

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(54) D. L. Kleinfelter and P. von R. Schleyer, *Org. Syn.*, 42, 79 (1962).

Table VIII. Composition of *endo*- (**3**) and *exo*-2-Chloronorbornane (**4**) Obtained from the Decomposition of *endo*-2-Norbornyl Chlorosulfite (**7**)

Solvent	Composition ratio[a] 3	4
Ether[b]	0.3	99.7
None	0.6	99.4
Pyridine	0.8	99.2

[a] See Table VI, footnote *a*. [b] See Table I, footnote *b*.

was obtained 0.471 g (65.8%) of *exo*-2-chloronorbornane (**4**), bp 158–160°, n^{22}D 1.4818.

B. To a solution of 1.02 g (0.005 mole) of **7** in 10 ml of ether was added 10 ml of 10% sodium carbonate. The organic layer was extracted and dried. The ether was evaporated under reduced pressure and a vpc analysis of the residue using a 10% diisodecyl phthalate (8 ft × 0.25 in.) column at 120° and a helium flow of 200 ml/min showed the ratio of *endo*-2-norborneol (**1**) to *exo*-2-chloronorbornane (**4**) was 22:78. The retention time was 7 min for **4** and 10 min for **1**.

3,3-Dideuterionorcamphor (14).[55] Into a 9-in., heavy-walled glass tube cooled to 0° was added 196.0 g (9.80 mole) of deuterium oxide[56] followed by cautious addition of 160.0 g (0.760 mole) of trifluoroacetic anhydride. After adding 61.6 g (0.560 mole) of norcamphor (**13**), the homogeneous solution was sealed and placed in a 2-l. Parr bomb containing 500 ml of benzene. The bomb was heated for 5 days at 125–135°. The product was added to a cold solution of 300 ml of water and 300 g of potassium carbonate, and the aqueous solution was extracted with 2-l. of pentane. The extract was dried, filtered, and concentrated under a Vigreux column until the pot temperature reached 40°. The last traces of solvent were removed by evacuating the sample for brief periods at 100–160 mm. The exchange was repeated and after work-up there was obtained 53.9 g of crude yellow solid which was sublimed to yield 50.5 g (80.6%) of white product. Nmr analysis showed the incorporation of 1.966 deuterium atoms per molecule (98.3% purity).

***endo*-2-Norborneol-2,3,3-d_3 (15).** To a well-stirred slurry of 0.647 g (0.00155 mole) of lithium aluminum deuteride[57] in 25 ml of dry ether under the most carefully controlled anhydrous conditions and cooled to 0° was added dropwise a solution of 5.191 g (0.0046 mole) of 3,3-dideuterionorcamphor (**14**) in 25 ml of ether. The mixture was stirred for 1 hr, and water was added dropwise to reduce the excess hydride. After addition of 25 ml of water, 25 ml of 10% hydrochloric acid was added. The mixture was extracted with ether, the ether layer dried over sodium sulfate, and the ether evaporated under reduced pressure to afford 5.205 g (98.8%) of product. A nmr analysis showed the incorporation of 2.886 deuterium atoms per molecule (96.2% purity).

***exo*-2-Norborneol-2,3,3-d_3 (16).** This compound was prepared by the method of Zweifel and Brown[27] by the addition of deuteriodiborane to 2,3-dideuterionorbornene (**21**)[58] followed by treatment with hydrogen peroxide. Nmr analysis showed that 1.848 atoms of deuterium per molecule for **21** (92.4% purity) by mass spectral analysis of **21** was as following: 8.1% d_3, 89.3% d_2, 2.4% d_1, and 0.1% d_0, and 2.73 atoms of deuterium per molecule for **16** (91.0% purity) were incorporated.

Acknowledgment. We wish to thank Thomas H. Kinstle, Iowa State University, Ames, for performing the mass spectral analyses on some of the compounds reported in this paper.

(55) We wish to thank J. P. Schaefer (University of Arizona, Tucson) for sending us this procedure which was slightly modified.

(56) Obtained from Bio-Rad Laboratories (99.85% D_2O).

(57) Obtained from Metal Hydrides Inc., minimum isotopic purity 97%.

(58) The synthesis of this compound is reported in the following paper.