Substituent Effects of Chlorine in Norbornanes[1]

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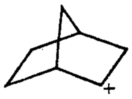
Hydrochlorinations of 1-chloronorbornene (**5**) and 2-chloronorbornene (**6**) afford 1,*exo*-3-dichloronorbornane (**4**) and 2,2-dichloronorbornane (**2**), respectively. Solvolytic and silver ion promoted ionization of **2**, **4**, and 1,*exo*-2-dichloronorbornane (**3**) have been examined. The results do not require the assumption of bridged intermediates. Hydroboration of **5**, followed by oxidation with alkaline hydrogen peroxide, results in a mixture of 1-chloro-*exo*-2-norbornanol (**11**, 38%) and 1-chloro-*exo*-3-norbornanol (**12**, 62%); this orientation differs from that observed in hydroboration of other allylic chlorides.

Much recent attention has been paid to the structure of the norbornyl cation and derivatives of it. In particular, debate has centered[2] on the question of whether the norbornyl cation is better represented as a σ-bridged ion, *i.e.*, a resonance hybrid of structures **1a** and **1b**, or as a rapidly equilibrating mixture of classical ions **1a** and **1b**. Saunders, Schleyer, and Olah have presented nmr evidence[3] that the parent norbornyl ion maintains symmetry down to $-120°$ in SbF_5–liquid SO_2, a result more compatible[2a] with a single species. On the other hand, no evidence compels the formulation of 2-phenyl-2-norbornyl[4] or even 2-methyl-2-norbornyl[5] cations as anything but classical. The norbornyl system is in fact constituted of a mixture of electronic and steric[2c] effects, readily perturbed by substituents.[6] For this reason, it is not clear whether data obtained with substituted norbornyl cations (except for substitution by deuterium[6a]) may be used with certainty as a diagnostic for structure of the parent ion. It is more appropriate to ask what evidence there is, for a given substituent, X, requiring formulation of X-substituted norbornyl cations, or better, the transition states leading to them,[7] as either classical or bridged. In this context and in view of the fact that previous studies of substituted norbornyl cations have not involved strongly electronegative substituents, we have studied the effect of substitution by chlorine upon several cationic reactions in the norbornyl series. Included were both solvolytic and silver ion promoted ionization of 2,2-dichloronorbornane (**2**), 1,*exo*-2-dichloronorbornane (**3**), and 1,*exo*-3-dichloronorbornane (**4**), the hydrochlorination of 1-chloro- and 2-chloronorbornenes (**5** and **6**, respectively), and the orientation in hydroboration of 1-chloronorbornene **5**. Hydroboration, although sensitive to electronic effects, does not involve carbonium ions;[8] it demonstrates the response of the system to inductive electron demand and was also used in structural correlations.



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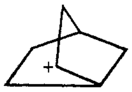

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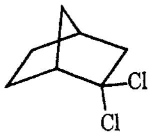

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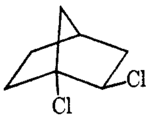

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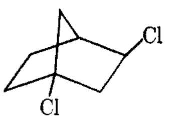

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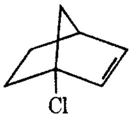

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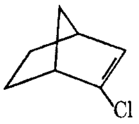

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Synthesis and Reactions of 1-Chloro- and 2-Chloronorbornenes.—Wilt and coworkers[9] have reported the slow rearrangement of **2** to an apparent equilibrium mixture consisting of 20% **2**, 64% **3**, and 16% 1,*endo*-2-dichloronorbornane (**7**) under the action of a slurry of aluminum chloride in carbon tetrachloride. It is not clear from the experimental data whether in fact a true equilibrium was obtained, since irreversible tar-forming reactions were taking place and no attempt was made to approach the equilibrium from **3** or **7**. We had independently observed the Lewis acid promoted isomerization of **2**. Under our conditions rearrangement takes a somewhat different course. When **2** is added to a *homogeneous solution* of aluminum chloride in dichloromethane,[10] a pale yellow solution is obtained. Work-up and analysis by vpc after 30 min shows both the *absence* of **2** and the presence of **3** and **7**, in 3:1 ratio; when the reaction time is extended to 24 hr, the mixture is much darker and the ratio of **3** to **7** is close to 1:1. Isomerization of **2** in toluene by the weaker Lewis acid, stannic chloride, is considerably slower than the aluminum chloride reaction, but is more specific, and is the synthetic method of choice for **3**. The only volatile product is **3**, and the conversion of **2** into **3** is conveniently monitored by vpc. We have been interested in this isomerization as a synthetic route to **3** but it is clear that product composition in the isomerate is quite dependent upon experimental conditions. These experiments suggest **3** as the initial

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[1] A portion of this research has been reported in preliminary form: A. J. Fry and W. B. Farnham, *Tetrahedron Lett.*, 3345 (1968).

[2] (a) P. D. Bartlett, "Non-Classical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) H. C. Brown and C. J. Kim, *J. Amer. Chem. Soc.*, **90**, 2082 (1968); (c) P. von R. Schleyer, *ibid.*, **89**, 701 (1967).

[3] (a) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964); (b) G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, **90**, 3882 (1968).

[4] H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1246, 1247, 1248 (1964).

[5] H. C. Brown and M.-G. Rei, *ibid.*, **86**, 5004 (1964).

[6] (a) J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, *ibid.*, **89**, 6938 (1967); (b) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *ibid.*, **90**, 3149 (1968). The latter paper describes significant differences in geometry between norbornane and 1,4-dichloronorbornane. The ability of the system to accommodate bridging ought to be a sensitive function of changes in geometry.[2]

[7] *Cf.* B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms—1965," John Wiley & Sons, Inc., New York, N. Y., 1966, Chapter 1.

[8] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

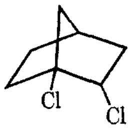
[9] J. W. Wilt, C. T. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968). We thank Professor Wilt for a preprint of his work.

[10] G. Baddeley, *Quart Rev.* (London), **8**, 355 (1954).

kinetically controlled product, and **7** as the product of subsequent isomerization. Solvolytic data on **2** and **3** (*vide infra*) support this belief: **2** ionizes far more easily than **3**, and **7** is undoubtedly even less reactive than **3**.[2]

Alkenes **5** and **6**[11] were readily available through dehydrohalogenation of **3** and **2**, respectively, under the action of potassium *t*-butoxide in dimethyl sulfoxide.

A recently described technique[12] for hydrochlorination was used, and, as others have reported,[13] low temperatures were necessary for rapid addition. Hydrochlorination (CCl_4, $-78°$) of **6** yields **2** quantitatively in less than 10 min; under the same conditions norbornene (**8**) is also converted rapidly and quantitatively into *exo*-norbornyl chloride (**9**), containing a trace (<1% by vpc analysis) of *endo*-norbornyl chloride.[14] 1-Chloronorbornene, however, when subjected to these conditions, is recovered unchanged after an 8-hr interval. This unreactivity is confirmed by competitive experiments. Hydrochlorination (CCl_4, $-78°$) of 50:50 mixtures of **5** and **6**, **5** and **8**, or **6** and **8** results in rapid quantitative addition of hydrogen chloride to **6** and **8** without any measurable reaction of **5**. However, use of methylene chloride as solvent did result in slow hydrochlorination of **5** (~90% reaction after 10 hr in a preparative run).[15] The major product is 1,*exo*-3-dichloronorbornane (**4**). This constituted somewhat more than 99.5% of the product by vpc analysis; only one other product (<0.5%), with the same retention time as **2**, was observed. Since this was formed in amounts too small to isolate, the possibility remains that it is the as yet unknown 1,*endo*-3-dichloronorbornane (this possibility was not pointed out in ref 1). Although 0.1% of **3** could have been detected, none was found. The *exo* attachment of chlorine in the major product was assigned on the basis of several reports of almost exclusive attachment of chlorine in hydrochlorination of norbornenes.[2c,16,17] Further structural evidence supporting structure **4** was obtained through dehydrohalogenation to **5**, and by silver nitrate assisted hydrolysis of **4** (*vide infra*) to 1-chloro-3-*endo*-norbornanol (**10**). The alcohol **10** was subsequently oxidized to 1-chloro-3-norbornanone (**14**).[18]



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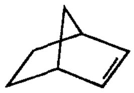

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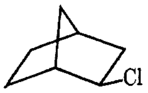

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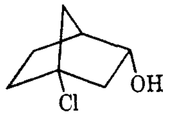

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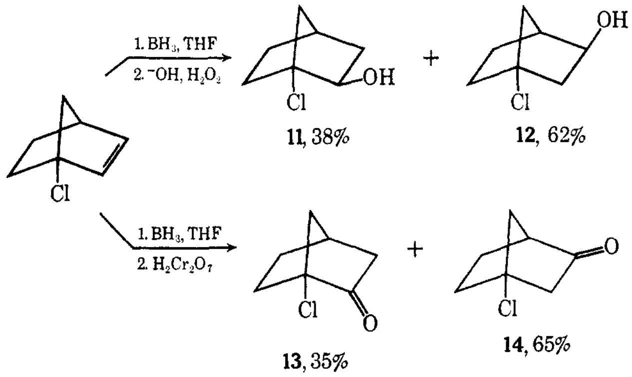
We have previously presented arguments[1] that the observed orientation in hydrochlorination of **5** is evidence against σ bridging in the transition state for hydrochlorination.

In brief, it was suggested that a bridged transition state would afford a mixture predominating in **2** and **3**, while the unbridged transition state would afford **4**. The Hammond postulate[19] was applied to suggest that the first *intermediate* in the hydrochlorination is likewise not bridged, but, since the relative energies of reactants and intermediate is not known, this postulate cannot be invoked here. Our data (*e.g.*, the orientation in addition to **6**) suggest that the transition states are cationic but do not allow statements about further stages along the reaction coordinate.

The unreactivity of **5** in hydrochlorination is worth further comment. We have found that allyl and crotyl chlorides and 1-chloro-1-butene are not hydrochlorinated measurably in 8 hr under conditions (CH_2Cl_2, $-78°$) where **5** (slowly) and **6** (rapidly) add hydrogen chloride. The markedly higher reactivity of both norbornenes relative to the acyclic alkenes is undoubtedly due to the strain in this ring system.[20] The slower rate of hydrochlorination of the haloalkenes is probably due to inductive electron withdrawal by halogen enhanced by hydrogen bonding of the halogen atom to hydrogen chloride.[21,22]

Whereas protonation of **5** in hydrochlorination occurs at the 2 position with >99.5% specificity, attachment of boron in hydroboration is slightly favored at the **3** position (Scheme I). It is reported that hydroborations of crotyl chloride[23] and 3-chlorocyclohexene[24] result in essentially complete addition of the boron

SCHEME I



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(11) N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M' Subramanian, *J. Amer. Chem. Soc.*, **85**, 3199 (1963).

(12) H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

(13) (a) L. Schmerling, *J. Amer. Chem. Soc.*, **68**, 195 (1946); (b) H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964).

(14) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, **88**, 4922 (1966).

(15) The function of methylene chloride in assisting hydrochlorination[12] is not clear; it has a lower melting point and higher dielectric constant than carbon tetrachloride, and also dissolves rather large amounts of hydrogen chloride at $-78°$. Any or all of these might contribute.

(16) (a) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 3901 (1967); (b) H. C. Brown and K. T. Lin, *ibid.*, **89**, 3898, 3900 (1967); (c) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, **88**, 4922 (1966).

(17) Professor Boris Franzus has carried out spin-decoupling nmr experiments on **4** which indicate that the proton at C-3 (>CHCl) is coupled not only to the vicinal protons at C-2 but to a third proton. The magnitude of this last coupling constant (J = 1.8–2.1 cps) is more consistent with H_{endo}–$H_{7\text{-}anti}$ long-range coupling than with H_{exo}–$H_{bridgehead}$ coupling, which is usually larger (3–4.3 cps). Dr. Franzus will report the spectral details, which also indicate some skeletal distortion in **4**, in a forthcoming manuscript.

(18) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Amer. Chem. Soc.*, **83**, 3998 (1961).

(19) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(20) T. Beier, H. G. Hanthal, and W. Pritzkow, *J. Prakt. Chem.*, [4] **26**, 304 (1964).

(21) A. J. Fry, *Tetrahedron Lett.*, 5853 (1968).

(22) R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **84**, 3221 (1962).

(23) H. C. Brown and R. M. Gallivan, Jr., *ibid.*, **90**, 2906 (1968).

(24) P. Binger and R. Koster, *Tetrahedron Lett.*, 156 (1961).

atom to the position β to chlorine, followed by elimination and rehydroboration.

This directive effect of chlorine was thought to be inductive.[23] However, our results suggest that the directive effect of chlorine must be more complex, since otherwise **11** and **13** would have been the exclusive products of hydroboration. It may be that coordination of the chlorine atom to the incoming hydroborating agent plays a role in the previously observed specific β orientations.[23,24] The ratio of **11** to **12** is similar to that obtained in the hydroboration of 5-*exo*-methoxynorbornene.[25] (Because of the hygroscopic nature of **11–13**, these are presumed structures, based on nmr and ir data; see the Experimental Section.)

The structural assignments for products **11–14** rest upon the fact that the ratios of **11**:**12** and **13**:**14** are the same within experimental error, as is reasonable, since the hydroboration step controls orientation and is the same for both. Since the major ketone is **14** (see the ir and nmr spectral data in the Experimental Section), the major alcohol must be **12**. The *exo* configuration in **11** and **12** is assigned by analogy to the hydroboration of other norbornenes.[8,25] The general shape of the >CHOH proton in the two alcohols supports this assignment.[26]

Silver Ion Assisted Hydrolyses.—Chlorides **3**, **4**, and **9** were suspended in aqueous silver nitrate at steam-bath temperatures until starting material, as monitored by vpc, had disappeared. The qualitative order of reaction was **9** > **4** > **3**; under these conditions, only **3** was incompletely reacted after 8 hr. The only product isolated from **3** was norcamphor. From **9** there were isolated *exo*-norbornanol (identical with synthetic material[8]) and a nitrate ester of unknown configuration, in the ratio of 3:1. From **4** there were again isolated both an alcohol and a nitrate, in ratio of 2:1. The alcohol must be 1-chloro-3-*endo*-hydroxynorbornane (**10**) from the fact that it may be oxidized to 4-chloronorcamphor **14** and the observation that the low-field proton (>CHOH) in its nmr spectrum appears at τ 6.15, while that in its epimer **12** appears at τ 6.55. Many studies have shown that *exo* protons occur at lower field than do *endo* protons for epimers in the norbornane series.[27]

The fact that the silver ion assisted hydrolysis of **4** proceeds with inversion of configuration, while the corresponding reaction with *exo*-norbornyl chloride **9** proceeds with retention of configuration (based on the observed geometry of the alcohols isolated) is consistent with a previously suggested mechanism involving gradations of S_N1 and S_N2 behavior for reactions of silver ion with alkyl halides.[28] For *exo*-norbornyl chloride, ionization should be much preferred[29] over S_N2 displacement by water or nitrate; this would result in over-all retention of configuration, as is observed. On the other hand, 1,3-dichloride **4** ionizes much less easily than **9** (see the next section on solvolytic experiments); apparently ionization is so unfavorable that carbon–chlorine bond breaking must require nucleophilic assistance by the solvent, this process resulting in inversion of configuration. Kornblum and Hardies[28] have also noted that, for reactions of alkyl halides with silver salts, inversion increases with decreased ionizing propensity of the halide.

The very slow reaction of **3** with silver nitrate deserves comment. In view of the fact that chlorine can stabilize a positive charge on the carbon to which it is attached[30] (*cf.* the hydrochlorination of 2-chloronorbornene and, in the next section, ease of ionization of 2,2-dichloronorbornane), the chlorine atom at the bridgehead in **3** should stabilize any positive charge appearing at C-1 during ionization. The low rate of reaction with silver ion suggests that bridging cannot be far advanced in the transition state for reaction of **3** with silver ion, if indeed it is involved at all.

Solvolytic Studies on Dichloronorbornanes.—Since a number of chloro-substituted *exo*-norbornyl chlorides were in hand, it was of interest to examine solvolytic routes to the corresponding chloronorbornyl cations. In order to make comparisons with rate data in the literature,[16a] kinetic measurements were made at 70.0° in 80% ethanol. For reasons to be described below, it was preferable to add a slight excess of sodium acetate and to titrate for chloride liberated. Because of the surprisingly slow solvolysis of **3** and **4**, only estimates of their reactivity could be obtained.

1. 2,2-Dichloronorbornane (**2**).—The solvolytic behavior of this substance was investigated in greatest detail. The products of solvolysis in 80% ethanol are 2-chloronorbornene **6** and norcamphor (**15**). When no sodium acetate was used, and the reaction rate was followed by titration of liberated acid with 0.020 *N* NaOH, a first-order plot was not obtained. It was then found that **6** is slowly converted into norcamphor in the presence of acid in 80% ethanol. An attempt was made to see if the hydrogen chloride catalyzed hydrolysis of **6** fit an autocatalytic kinetic expression,[31] but no simple rate law fit the data: an infinity titer was never obtained, and the amount of acid present actually began to decrease after 500 hr. Cristol and Caple[32] have likewise noted slow consumption of hydrogen chloride by ethanol solutions, presumably as a result of ethyl chloride formation.[33] Because of the complications in making kinetic measurements in the presence of acid, a small excess of sodium acetate was added, and a good first-order plot was obtained, in a manner to be shown below. The percentage of **6** in the products (**6** and **15**) remained constant at 56 ± 1% (by vpc) throughout the solvolysis. It is clear that **6** is not formed *via* an E2 reaction involving **2** and sodium acetate, for the following reasons. First, **6** is present in the same proportion in the early stages of solvolysis carried out in the absence of sodium acetate, and, second, the sodium acetate was not present in high enough initial concentration to yield a pseudo-first-order kinetic expression.

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[25] P. J. Stang and P. von R. Schleyer, paper P-192 presented at the 155th National Meeting of the American Chemical Society, April 1968. We thank Professor Schleyer for a manuscript describing his work.

[26] W. C. Baird, Jr., *J. Org. Chem.*, **31**, 2411 (1966), and references therein.

[27] *E.g.*, T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 3212 (1963).

[28] N. Kornblum and D. E. Hardies, *ibid.*, **88**, 1707 (1966).

[29] Schaefer, *et al.*, have commented on the difficulty in forcing the S_N2 pathway on *exo*-substituted norbornanes, even in nonpolar solvents.[6a]

[30] N. C. Deno, G. W. Holland, Jr., and T. Schulze, *J. Org. Chem.*, **32**, 1496 (1967).

[31] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961.

[32] S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).

[33] Under neutral conditions olefin **6** reacts less than 1% (vpc analysis) in 560 hr.

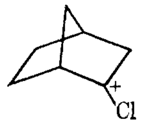
Formation of **6** from **2** requires liberation of one chloride ion, while formation of norcamphor results in liberation of two chloride ions per mole of **2** reacted. Since the reaction is followed by titration of chloride generated, a modification of the usual first-order kinetic expression must be used. It may be shown that, if **2** is disappearing by a first-order process, expressions 1 and 2 should hold, where a is the initial concentration of

$$\ln (a - by) = kt \qquad (1)$$

$$b = \frac{100}{(\%\ \mathbf{6})(1) + (\%\ \mathbf{15})(2)} \qquad (2)$$

dichloride, y is the concentration of chloride ion at time t, and $1/b$ is the number of moles of chloride ion formed per mole of **2** reacted. From the measured product ratio, and also from an infinity titration, $b = 0.69$, and in fact, only for this value of b is the plot of the titration data a straight line. The value calculated is $k = (2.47 \pm 0.04) \times 10^{-5}$ sec^{-1} (Figure 1). Dichloride **2**, therefore, solvolyses 5.5 times faster than *exo*-norbornyl chloride **9** [$k = (4.47 \pm 0.04) \times 10^{-6}$ sec^{-1}].[16a]

The increased rate of solvolysis of **2** over **9**, formation of **6** and **15** as products, and the constant ratio of **6**:**15** thoughout the reaction are most economically interpreted in terms of rate-determining ionization of **2** to the α-chlorocarbonium ion **16**, which would then partition itself between proton loss to afford **6** and reaction with solvent to yield, ultimately, norcamphor. Queen and Robertson[34] have concluded, from measurements of heat of activation and from deuterium kinetic isotope effects, that several 2,2-dihalopropanes solvolyze in water by the SN1 mechanism, and Streitweiser[35] has interpreted the net accelerating effect of an α-chloro substituent on the rates of ionization of alkyl halides as a resultant of inductive electron withdrawal and electron release by the resonance effect. The synthesis of deuterium-substituted analogs of **2** is in progress, in order to gain further information on the detailed course of solvolysis.



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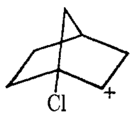

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2. 1,*exo*-2-Dichloronorbornane (3) and 1,*exo*-3-Dichloronorbornane (4).—When 1,*exo*-2-dichloronorbornane (**3**) was heated in 80% ethanol at 85° for 480 hr no norcamphor or other product could be detected by vpc. Assuming that 0.5% product could have been detected (control experiments corroborated this), it may be concluded that less than 0.5% reaction occurred. At 70.0°, less than 0.2% reaction (by titration) occurred in 795 hr. The *upper limits* for the first-order rate constants for solvolysis of **3** based on these data are 7×10^{-10} sec^{-1} at 70° and 2.8×10^{-9} sec^{-1} at 85°. *exo*-Norbornyl chloride **9** solvolyzes, therefore, faster than **3** by a factor of at least 6.4×10^{3} at 70° and 7×10^{3} at 85.[16a] These rate constants correspond to half-lives at 70° for **9** and **3** of 42 hr and >30 yr.

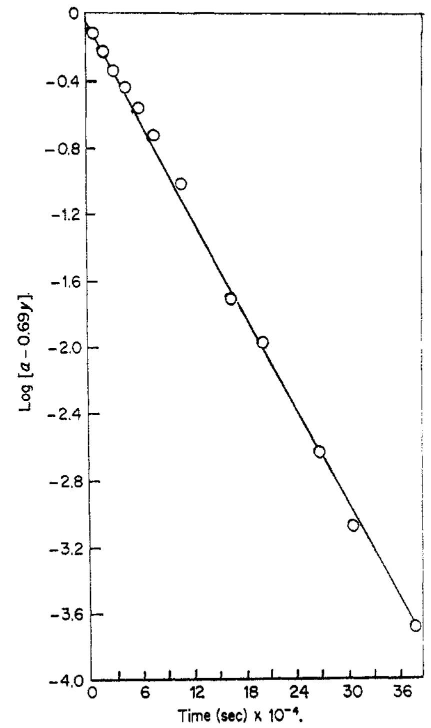

Figure 1.—Plot of the logarithm of the concentration of 2,2-dichloronorbornane *vs.* time in 80% ethanol at 70.0°, a = 0.171 *M*.

Although solvolysis of 1,*exo*-3-dichloronorbornane (**4**) does proceed, as evidenced by titration and vpc analysis, it is also very slow; it was followed to only 5% reaction, which took 530 hr. A very rough approximation of the first-order rate constant was made with $k = 2.7 \times 10^{-8}$ sec^{-1}. Because of experimental error in determination of chloride ion and the fact that only 5% of the starting material had reacted, the only significant part of the rate constant is the order of magnitude 10^{-8}. Norbornyl chloride ($k = 4.47 \times 10^{-6}$ sec^{-1}), therefore, ionizes faster than **4** by a factor of $(2 \pm 1) \times 10^{2}$.

In order to assess the effect of the bridgehead chlorine in **3** upon its rate of ionization, one might imagine two extremes for the ionization transition state. If it were unbridged (**17**) the only effect of chlorine would be inductively destabilizing. If, on the other hand, bridging were far advanced, then the resonance effect would allow stabilization and hence rate acceleration. The actual situation could be anywhere between these two extremes, but, to the extent that bridging is important, the rate of ionization of **3** should be larger than that expected on purely inductive grounds. The low observed rate demonstrates that bridging, at the least, cannot be far advanced in the transition state for ionization. There remains the question whether there is any contribution at all from bridging in the transition state. The minimum value of 7×10^{3} for the ratio of solvolysis rates of **9** and **2** may be compared to the observation that *t*-butyl chloride solvolyzes 4×10^{3} times faster than 1,2-dichloro-2-methylpropane (**18**) in 80% ethanol at 79°,[36] suggesting the naive interpretation that we are observing the extreme case of ionization without bridging. In fact, however, this conclusion is

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[34] A. Queen and R. E. Robertson, *J. Amer. Chem. Soc.*, **88**, 1363 (1966).

[35] A. Streitweiser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 102.

[36] See ref 35, p 124. The rate depression upon substitution by chlorine is quite close to that predicted by a Taft treatment, suggesting that chlorine does not participate in the solvolysis of **18**.

not warranted, for the 1,3-dichloride **4** solvolyzes substantially more slowly than one would expect using a Taft treatment[37] with commonly observed values for σ^* and ρ^*, and the attenuation of the inductive effect through an extra bond. Since the norbornyl system may therefore be unusually sensitive to inductive effects, we cannot predict the rate of ionization expected for **3** on purely inductive grounds. We can say that these data at present do not require assumption of bridging in ionization of **3**. Clearly there is a need for much more data concerning the response of the norbornyl system to inductive effects of substituents, particularly those which are strongly electronegative.

Experimental Section[38]

2,2-Dichloronorbornane (**2**) was prepared by the method of Bixler and Niemann.[39] The product was >99.8% pure (trace of **6**) by vpc (Zonyl E-7, 120°, and SE-30, 125°). It was purified by preparative vpc for kinetic experiments. The nmr spectrum consists of two multiplets from τ 7.0 to 7.3 and from 8.0 to 9.0 (relative areas 1:4, respectively).

1,*exo*-2-Dichloronorbornane (**3**).—Stannic chloride, 6.5 g (25 mmol), was added to a solution of 20.0 g (122 mmol) of **2** in 100 ml of toluene, and the mixture stirred at 55° for 30 hr, after which time vpc (Zonyl E-7, 120°) showed the absence of **2**. Following the addition of 100 ml of pentane, the mixture was washed with 100 ml of cold 25% sulfuric acid and two 150-ml portions of water. A small amount of black insoluble material was filtered, the organic extracts were dried over magnesium sulfate, and the solvents were distilled through a glass helix packed column. Distillation afforded 15.6 (78%) of **3**: bp 103.5–105° (26–28 mm); mp 32–33° [lit.[9] bp 77° (11 mm)]; homogeneous by vpc (Zonyl E-7, 110°).

1-Chloronorbornene (**5**).—To a solution of 11.2 g (68 mmol) of **3** in 60 ml of dimethyl sulfoxide was added 11.0 g (98 mmole) of potassium *t*-butoxide. The mixture was stirred magnetically for 24 hr at room temperature. After dilution with 250 ml of water, the mixture was extracted with 200 ml of pentane. The aqueous phase was diluted with 100 ml of water and extracted twice with 150-ml portions of pentane. The combined pentane extracts were washed three times with water and dried over magnesium sulfate. Pentane was separated by distillation through a glass helix packed column. Distillation afforded 6.0 g (69%) of **5**: bp 86–88° (130 mm) [lit.[9] 75.5–77.5° (95 mm), 68%]. This material was homogeneous by vpc (Carbowax 20M, 95° and SE-30, 110°).

Hydrochlorination of 6.—A procedure described previously[12] was used, except that instead of the glass-tipped buret and valve of the analytical unit, the valve of the preparative unit was used. Contact of the concentrated hydrochloric acid with metal was avoided by connecting a glass-tipped syringe with the mercury in the valve by a flexible Teflon needle (Hamilton Co.) piercing the rubber septum of the valve. The apparatus was flushed with hydrogen chloride and chilled to −78°. A solution of 0.40 g of **6** and 1 ml of carbon tetrachloride was added; uptake of hydrogen chloride began immediately and had ceased after 10 min. Vpc (Zonyl E-7, 115°) indicated complete conversion into **2**; the same result was obtained using dichloromethane as solvent.

Competitive Hydrochlorination Experiments.—An equimolar mixture of **5** and **6** in carbon tetrachloride was treated as previously described. Examination by vpc after 10 min showed only **5**, **2**, and a trace of **7**. Similar treatment of a mixture of **5** and **8** showed the presence of only **5** and *exo*-norbornyl chloride (**9**). An equimolar mixture of **6** and **8** was converted completely into **2** and **9** under these conditions.

1,*exo*-3-Dichloronorbornane.—A solution of 4.5 g of **5** in 10 ml of dichloromethane was allowed to react according to the above procedure. After 10 hr at −78°, the mixture was washed with 20 ml of water and dried over magnesium sulfate. After distillation of the solvent and a small amount of unreacted **5**, vpc analysis (Zonyl E-7, 130°) indicated only two components, 1,*exo*-3-dichloronorbornane **4** (>99.5%) and a peak with the same retention time as **2**. The nmr spectrum of **4** consists of two multiplets, at τ 6 and between 7.3 and 8.8 (relative areas 1:9); the ir spectrum of **4** differs considerably from those of **2** and **3** between 8.0 and 11.6 μ; the strongest peaks appeared at 8.38, 8.58, 9.48, 9.88, 10.15, 10.50, 10.88, 11.00, and 11.56 μ.

Anal. Calcd for $C_7H_{10}Cl_2$: C, 50.93; H, 6.11; Cl, 42.96. Found: C, 50.99; H, 6.07; Cl, 43.18.

Hydroboration–Chromic Acid Oxidation of 5.—To a solution of 1.0 g of **5** in 1 ml of tetrahydrofuran at 0° was added, through a rubber septum, 3.5 ml of a 1.0 *M* solution of diborane in tetrahydrofuran (Metal Hydrides, Inc.). After 15 min, 0.5 ml of water was added, followed by dropwise addition of a solution of 1.72 g of sodium dichromate dihydrate and 1.30 ml of concentrated sulfuric acid in 7 ml of water. After 1.5 hr, 10 ml of water was added, and the mixture was extracted with ether. The ether extracts were washed three times with water and dried over magnesium sulfate; the solvent was then removed at the rotary evaporator. Vpc (SE-30, 135°) showed two products in 65:35 ratio. Theses were separated by preparative vpc and possessed distinctly different spectral properties. The major ketone, 1-chloro-3-norbornanone, **14**, had three multiplets in its nmr spectrum at τ 7.6, 7.9, and 8.3 (relative areas 1:2:6) and characteristic ir bands at 7.78, 8.15, 8.21, 8.54, 8.65, 9.38, 9.92, 10.10, 10.48, and 10.60 μ; these properties are identical with those reported for **14**,[18] except that the carbonyl appears at 5.70 rather than 5.73 μ. The minor ketone, 1-chloro-2-norbornanone, **13**, had the following characteristics: nmr, two multiplets at τ 7.3 and from 7.6 to 8.5 (relative areas 1:8.5); ir 5.65 (C=O), 7.70, 8.48, 9.21, 9.75, 10.44, and 11.47 μ.

Hydroboration–Alkaline Hydrogen Peroxide Oxidation of 5.—To a solution of 2.3 g of **5** in 4.6 ml of tetrahydrofuran was added 4.6 ml of a 1 *M* solution of diborane in tetrahydrofuran. After 15 min, there were added 1.9 ml of 3 *M* sodium hydroxide and 1.4 ml of 50% hydrogen peroxide. The products were isolated as in the preceding reaction. Vpc (SE-30, 135°) showed two solid products in the ratio of 62:38. These were separated by preparative vpc. The nmr spectrum of the minor isomer 1-chloro-2-*exo*-norbornanol, **11**, mp 75.5–77.5°, consists of a multiplet at τ 6.3, singlet at 7.05, and multiplet from 7.7 to 9.0 (relative areas 1:1:9); the nmr spectrum of the major alcohol 1-chloro-3-*exo*-norbornanol, **12**, mp 86–87°, consists of a multiplet centered at τ 6.55, singlet at 7.3, and multiplet from 7.75 to 9.0 (relative areas 1:1:9, respectively). The singlets at τ 7.05 and 7.3 in the two spectra are concentration dependent and are assigned to hydroxyl protons in the two alcohols. Microanalytical data were unsatisfactory, since the two alcohols were hygroscopic.

Silver Nitrate Assisted Hydrolysis of 4.—To a solution of 0.125 g (0.73 mmol) of silver nitrate in 0.3 ml of water was added 0.10 g (0.61 mmol) of **4**. The flask was stopped and heated on the steam bath with frequent vigorous stirring. After 3 hr, vpc analysis indicated that **4** had completely reacted. After cooling and extraction with ether, the ether extracts were washed with water and dried over magnesium sulfate, and the solvent was removed at the rotary evaporator. Vpc analysis (SE-30, 130°) showed two products in ~2:1 ratio. The minor isomer had an nmr spectrum consisting of a multiplet at τ 5.1 and another multiplet from 7.35 and 8.70 (relative areas 1:9.6); the strongest peak in the ir spectrum appears at 6.1 μ ($-ONO_2$). The major product, 1-chloro-3-*endo*-norbornanol (**10**), had ir absorption at 2.78, 3.00, and 9.00 μ (>CHOH); its nmr spectrum consisted of a multiplet at τ 6.15 (>CHOH), concentration-dependent singlet at ~6.5 (OH), and a multiplet from 7.55 to 8.75 (relative areas 1:1:9.3). The vpc retention time of **10** was clearly different from that of **12**.

Silver Nitrate Assisted Hydrolysis of 9.—*exo*-Norbornyl chloride (prepared by hydrochlorination of **8**) was treated with aqueous silver nitrate as above. Vpc analysis (SE-30, 125°) showed two products, in the ratio of 3:1. The major product

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[37] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, Chapter 13.

[38] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Nuclear magnetic resonance spectra were recorded in carbon tetrachloride on a Varian A-60A spectrometer, relative to external tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer Model 137 infrared spectrophotometer. A Varian Aerograph Model 90-P gas chromatograph was used for preparative and analytical separations. Three columns were used: a 2 ft × 0.25 in. column packed with 15% Zonyl E-7 on 20/40 mesh Fluoropak 80; a 5 ft × 0.25 in. column packed with 20% SE-30 on 60/80 mesh Chromosorb W; and an 18 in. × 0.25 in. column packed with 15% Carbowax 20M on 20/40 mesh Fluoropak 80. Column temperatures are reported for individual experiments.

[39] R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958).

was identical with a sample of *exo*-norbornanol prepared by hydroboration of norbornene.[8] The low-field proton (<CHOH) in the nmr spectrum of each alcohol appeared at τ 6.38. The minor isomer was a nitrate, ir 6.1 μ ($-ONO_2$).

Silver Nitrate Promoted Hydrolysis of 3.—1,*exo*-2-Dichloronorbornane (**3**) was treated with aqueous silver nitrate as described above. After 8 hr vpc analysis (SE-30, 130°) showed the presence of norcamphor and a small amount of unreacted **3**.

4-Chloronorcamphor (14) from 1-Chloro-3-*endo*-norbornanol (10).[8]—To a solution of 0.21 g of **10** in 0.7 ml of ether was added dropwise a solution of 0.15 g of sodium dichromate dihydrate and 0.11 ml of concentrated sulfuric acid in 0.75 ml of water. After 45 min at room temperature, 10 ml of ether was added. The organic phase was washed successively with aqueous sodium bicarbonate and water and dried over magnesium sulfate, and the solvent was removed at the rotary evaporator. Analysis by vpc showed two products (ratio of *ca.* 95:5). The major product was isolated by preparative vpc; its nmr and ir spectral properties and vpc retention time were identical with those of **14**,[18] except for the slight difference in carbonyl position already noted.

Solvolysis of 2,2-Dichloronorbornane (2).—A solution of 2.8025 g (17.10 mmol) of **2** and 2.3569 g (28.73 mmol) of sodium acetate trihydrate dissolved in 80% ethanol–20% water (v/v) was diluted to 100 ml in a volumetric flask. Aliquots (5 ml) were injected into soft glass ampoules which were then chilled, sealed under vacuum, and immersed in a constant-temperature bath at 70.0 ± 0.1°. Ampoules were titrated with 0.0200 *M* silver nitrate by Fajan's method, using dichlorofluorescein as indicator.[40] Analysis by vpc (SE-30, 125°) showed the products to be **6** (56 ± 1%) and **15** (44 ± 1%); the ratio was constant throughout the reaction.

Attempted Solvolysis of 1,*exo*-2-Dichloronorbornane (3).—A solution of 1.0 g of **3** in 20 ml of 80% ethanol was maintained at 85° for 480 hr. No liberated acid could be detected by titration with base. Analysis by vpc (SE-30, 140°) showed only **3**. Aliquots (5 ml) of a solution of 0.6943 g of **3** in 25 ml of 80% ethanol were sealed in ampoules as above. Titration of the ampoule opened after 795 hr indicated less than 0.2% reaction.

Attempted Solvolysis of 1,*exo*-3-Dichloronorbornane (4).—A solution of 1.6017 g (9.766 mmol) of **4** and 0.8040 g (9.800 mmol) of sodium acetate was diluted to 100 ml in 80% ethanol and sealed in ampoules as above. The contents of the ampoule titrated with 0.0100 *M* silver nitrate after 530.5 hr at 70° required 2.70 ml of titrant. The rate constant based on this titration (*ca.* 5% reaction) was based on the assumption that the impurity (0.4%) (*vide supra*) consisted of 2,2-dichloronorbornane **2**.

Registry No.—**2**, 19916-65-5; **3**, 15019-72-4; **4**, 19916-67-7; **5**, 15019-71-3; **6**, 694-93-9; **11**, 19916-70-2; **12**, 19916-71-3.

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[40] H. H. Willard and N. H. Dean, "Elementary Quantitative Analysis," 3rd ed, D. Van Nostrand Co., New York, N. Y., 1940, p 169.

Cleavage of Hindered Aromatic Ethers. Kinetics[1]

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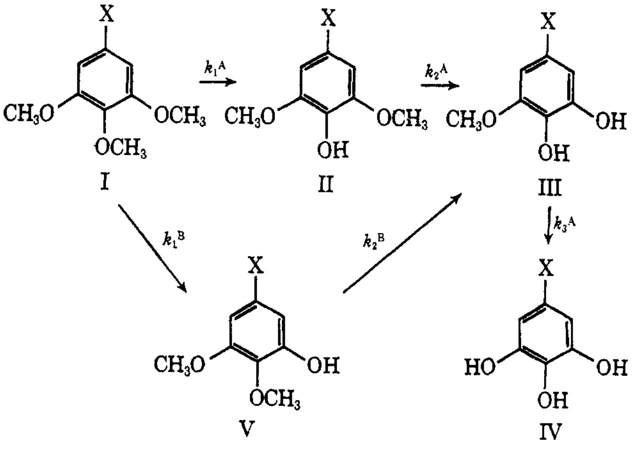
The rates of ether cleavage by HBr in glacial acetic acid at 76° for trisethers and related monoethers are correlated by a $\rho\sigma$ plot. It is concluded that the enhanced rate of cleavage of 1,2,3-trimethoxybenzenes is too large to be accounted for by electrostatic substituent effects and occurs mainly because of the enhanced basicity of the central methoxyl as it is sterically twisted out of the plane of the benzene ring. The role of nonbonded interactions is discussed.

It is well known that trisethers with structure I, where X can be either an electron-attracting or electron-donating group, are cleaved by various acidic reagents to give largely II along with slight amounts of III and IV but little if any V[2-4] (Scheme I). Three different rationalizations can be offered. The generally accepted view[5] is that the middle methoxyl is crowded out of the plane of the benzene ring. This involves an unspecified combination of steric alteration of nonbonded interactions and enhanced basicity of the central methoxyl due to partial loss of conjugation. Brossi, *et al.*,[6] in discussing the ether cleavage of cactus alkaloid isoquinoline analogs of I, emphasized the second component involving enhanced basicity. A third possibility is that the rates are normal and determined solely by the accepted electronic effects of all ring substitutents. Although much qualitative product data are available for this reaction, there are only

SCHEME I



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[1] Taken in part from the M.S. dissertation submitted by M. A. Seager to the Cornell Graduate School, Sept 1966.

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