was dissolved in 25 ml of 15% perchloric acid which had been brought to pH 2.5 by careful addition of 2 *N* sodium hydroxide while cooling the solution in an ice bath. An aqueous solution of 0.63 g of sodium nitrite in 10 ml of water was added slowly, maintaining the pH between 2.3 and 2.7. The solution was then heated to 60° for 6 hr and cooled, and saturated sodium chloride solution was added. The product was extracted with ether, washed with water, and dried. Filtration to remove the drying agent, and removal of the solvent on a rotary evaporator followed by preparative glpc of a small amount of the reaction mixture on a 6-ft 15% Carbowax 1500–3% KOH on 60–80 Chromosorb G column at 130° gave **23**: nmr (CCl_4) τ 7.6–8.9 (broad envelope of ring protons), no proton on the carbon bearing the hydroxyl group, 8.6 (s, hydroxyl); ir 3510 (OH stretch), 1125 cm^{-1} (tertiary CO stretch).

Acid-Catalyzed Rearrangements of Products of Solvolysis of 6. The products of solvolysis of **6** were subjected to nonbuffered solvolysis conditions to determine which were stable. The alcohols were each placed in a sealed tube in a solution of 0.025 *M* *p*-nitrobenzoic acid in 70% aqueous dioxane and heated at 230° [39] for 2 hr. The solutions were analyzed directly by glpc on a 10% Carbowax 20M-KOH on 60–80 Chromosorb G column at 160°, and retention times were compared to authentic samples. Compounds **21**, **13**, **22**, and **23** were found to be stable under these conditions. Compound **4** rearranged to give **21** and **22** as major products (*ca.* 2:1), a small amount of **13**, and traces of **12** and **23**. Compound **12** rearranged to give **22** and **13** as major products (*ca.* 1.2:1) and a small amount of **23**.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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[39] A batch of Dow-Corning 210-H Fluid was used.

1,2-, 1,4-, 1,5-, and 1,6-Halogen Participation in the Trifluoroacetolysis of Primary Alkyl Nosylates

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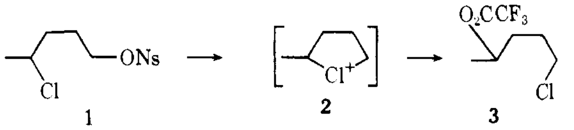
Contribution from the Department of Chemistry, St. Louis University, St. Louis, Missouri 63156. *Received July 1, 1970*

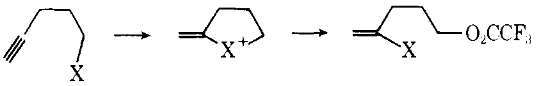
Abstract: The trifluoroacetolyses of the following *p*-nitrobenzenesulfonates were studied: 2-chloro-1-propyl, 3-chloro-1-butyl, 4-chloro-1-pentyl, 5-chloro-1-hexyl, 6-chloro-1-heptyl, and 5-bromo-1-hexyl. Trifluoroacetolysis of 2-chloro-1-propyl and 4-chloro-1-pentyl nosylates gave substantially quantitative 1,2- and 1,4-halogen shifts. The extent of halogen shift was reduced to 90% for 5-chloro-1-hexyl nosylate and ~17% for 6-chloro-1-heptyl nosylate. Rate accelerations owing to chlorine participation by factors of 2000, 760, and 7.1 were estimated from analysis of measured rates for 2-, 4-, and 5-chloro-1-alkyl nosylates, respectively. Halonium ion intermediates having three-, five-, six-, and seven-membered rings are postulated to explain the halogen shifts and rate accelerations observed.

In a preliminary communication we have reported[1] that trifluoroacetolysis of the primary nosylate (*p*-nitrobenzenesulfonate) **1** leads (presumably *via* halonium ion **2**) to the product of 1,4-halogen shift **3** to the extent of 99.5% (eq 1). The first 1,5-halogen shifts also were reported in the analogous reactions of the homologs 5-chloro- and 5-bromo-1-hexyl nosylate. Based on these results, it seemed probable that the combination of a primary leaving group, a secondary halide participating group, and a weakly nucleophilic solvent constitutes the most favorable system for the observation of halogen participation yet found. Accordingly, we have extended the study, as reported here, to include determinations of reaction rates and additional halogen shift reactions. The results uphold the promise shown in the preliminary studies.



1 2 3 (1)

Previous studies from our laboratories established that halogen participation of the type mentioned above is not uncommon. Reaction of 5-halo-1-alkynes with trifluoroacetic acid, for example, gave predominantly halogen-shifted products (eq 2).[2] Alkenes showed evidence for an extent of 1,4-halogen participation in reaction with trifluoroacetic acid similar to that in alkynes,[3]



(2)

whereas cyclopropane ring openings in trifluoroacetic acid showed less participation.[4] On the other hand, solvolyses of ω-halo secondary tosylates showed more participation than the comparable reactions of alkynes.[5] These secondary tosylate–primary chloride solvolyses, which are closely related to the reactions to be reported in this paper, resulted in no halogen shifts, however. 5-Chloro-2-pentyl tosylate, for example, was postulated (from rate evidence) to react predominantly *via* the ion **2** (eq 1), which opened to the unshifted product **3**. Furthermore, the rate accelerations owing to 1,4-halogen participation in these tosylate reactions were evident only if substantial allowances for inductive effects in the nonparticipation (normal solvolysis) reaction

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(1) (a) P. E. Peterson and J. F. Coffey, *Tetrahedron Lett.*, 3131 (1968); (b) *cf.* W. S. Traynovsky, G. L. Smyser, and M. D. Doyle, *ibid.*, 3127 (1968).

(2) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *J. Amer. Chem. Soc.*, **92**, 2834 (1970), and earlier references cited therein.

(3) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *ibid.*, **87**, 5163 (1965).

(4) P. E. Peterson and G. W. Thompson, *J. Org. Chem.*, **33**, 968 (1968).

(5) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Amer. Chem. Soc.*, **89**, 5902 (1967).

were made. The observation of three-membered ring halonium ions[6] and, later, five-membered ring[7] halonium ions by nmr spectroscopy of SbF_5–SO_2 solutions provided satisfying supplementary evidence supporting the possibility that halonium ion intermediates may be formed in the solvolytic reactions reviewed above.

Description and Results

The primary nosylate–secondary halides shown in the first six entries of Table I were synthesized, and the rate constants (Table I) for trifluoroacetolysis were measured by quenching samples in moist isopropyl alcohol, followed by ultraviolet spectrophotometry. In principle these nosylates could react *via* intermediate three-, four-, five-, six-, and seven-membered ring chloronium ions, respectively. In addition 4-chloro- and 4-fluoro-1-butyl nosylates were studied, as were the unsubstituted nosylates, ethyl, 1-hexyl, and isopropyl.

Table I. Rate Constants for Trifluoroacetolysis, 60°

Nosylate	$k \times 10^5$, sec^{-1} [a]
2-Chloro-1-propyl	~0.09
3-Chloro-1-butyl	0.0064
4-Chloro-1-pentyl	52
5-Chloro-1-hexyl	1.62
6-Chloro-1-heptyl	0.39
4-Chloro-1-butyl	11.7
4-Fluoro-1-butyl	0.052
5-Bromo-1-hexyl	5.1
Ethyl	0.040
Ethyl–0.125 *M* $NaOCOCF_3$	0.078
Isopropyl	750[b]
1-Hexyl	0.51

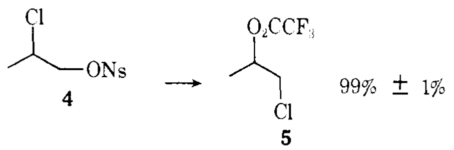
[a] At 0.003 *M* nosylate and 0.004 *M* sodium trifluoroacetate concentrations except where indicated otherwise. [b] Extrapolated from the values 22×10^{-5} at 25° and 110×10^{-5} at 40°. These values give $\Delta H^{\neq} = 19.3$ kcal/mol and $\Delta S^{\neq} = -10.5$ eu.

Table II. Products of Trifluoroacetolyses

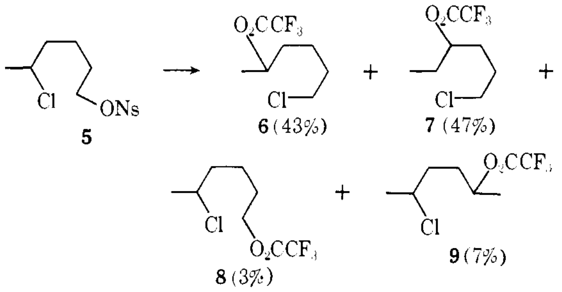
Nosylate	Trifluoroacetates, % of total		
1-Hexyl[a]	1-Hexyl	12	
	2-Hexyl	50	88
	3-Hexyl	38	
4-Chloro-1-pentyl[a]	4-Chloro-1-pentyl	0.5	
	5-Chloro-2-pentyl	99.5	
5-Chloro-1-hexyl[a]	5-Chloro-1-hexyl	3	
	5-Chloro-2-hexyl	7	
	6-Chloro-2-hexyl	43	90
	6-Chloro-3-hexyl	47	
6-Chloro-1-heptyl[b]	Primary chlorides[c]	~17	
5-Bromo-1-hexyl[b]	Primary bromides	93	

[a] Data from glc analysis of the solvolysis products. [b] Data from the nmr spectrum of the reacted solvolysis mixture. [c] Presumed products of the 1,6-chlorine shift. See Experimental Section for additional data.

In Table II products of reaction are given. In addition to the high percentage of halogen-shifted product obtained from 4-chloro-1-pentyl nosylate (eq 1) and 2-chloro-1-propyl nosylate (eq 3) the formation in major amounts of 1,5-halogen-shifted products **6** and **7** from 5-halo-1-hexyl halides is noteworthy. As shown in eq 4, the product **7** is both halogen shifted and hydrogen shifted. The formation of 17% of primary chlorides,



(3)



(4)

presumably the product of 1,6-halogen shift, from 6-chloro-1-heptyl nosylate also is noteworthy as the first observed such shift.

The Halogen Participation Reaction. In order to use the rate data in estimating the extent of halogen participation we endeavored, as previously,[5] to effect the Winstein separation of the rate constant for reaction into components, k_Δ, for reaction involving neighboring halogen participation, and k_s, for the "normal" solvolysis reaction.[8] In close analogy with our previous analysis of the secondary tosylate rates,[5] we assumed that the rate constant k_X for the reaction of 3-chloro-1-butyl nosylate has a negligible k_Δ component as a consequence of the difficulty of forming a four-membered ring halonium ion.[9] Then $\log k_X - \log k_H \equiv \Delta \log k$ is a measure of the inductive effect upon the normal solvolysis rate. The rate constant k_H for reaction of an unsubstituted nosylate may be taken to be that of 1-hexyl nosylate pending further discussion. Based on the assumption that the inductive effect is attentuated by a constant factor, ϵ, per methylene group, we may write, as in the previous paper,[5] $\Delta \log k_n = \epsilon^{n-m}(\Delta \log k_m)$ where n and m = numbers of carbon atoms in the aliphatic chains of the halogenated tosylates whose inductive effects are compared. Then

$$\log(\Delta \log k_n) = (\log \epsilon)(n - m) + \log(\Delta \log k_m)$$

cf. $y = mx + b$.

In Figure 1 the linearity of the plot from which $\log \epsilon$ was evaluated from points for 3-chloro-1-butyl nosylate, 4-fluoro-1-butyl nosylate, and 6-chloro-1-heptyl nosylate is illustrated. The rate constant for the latter compound was reduced by 17% to correct for chlorine participation, based on the amount of chlorine shift shown in Table II. The plotted point for 4-fluoro-1-butyl nosylate was obtained by adjustment of the experimental $\log k_H/k_X$ value to that expected for a chloro substituent, based on the Hammett–Taft equation, $\log k_H/k_X = -\rho_I\sigma_I$.[10] The absence of fluorine participation is in-

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(6) (a) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); (b) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1969), and earlier references cited therein.

(7) G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968).

(8) For leading references see J. M. Harris, F. L. Schadt, P. von R. Schleyer, and C. J. Lancelot, *ibid.*, **91**, 7508 (1969).

(9) The postulated absence of chlorine participation in 3-chloro-1-butyl nosylate solvolysis (not verified because of the extreme slowness of reaction) is strongly supported by the absence of kinetically significant chlorine shift in the faster trifluoroacetolysis of 3-chloro-1-butyl trifluoromethanesulfonate (P. E. Peterson and W. Boron, unpublished work).

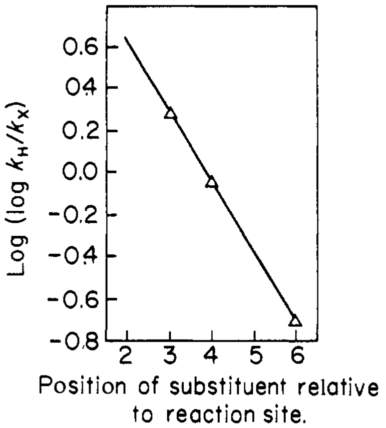


Figure 1. Attentuation plot for trifluoroacetolysis rates. Inductive effects observed in the solvolysis of 3-chloro-1-butyl, 4-fluoro-1-butyl, and 6-chloro-1-heptyl nosylates, respectively (compared to 1-hexyl nosylate), are plotted *vs.* the number of atoms separating the nosylate group from the halogen (upper left to lower right). The log (log) function is explained in the text of this paper.

ferred from the recently reported[2] absence of fluorine shift upon solvolysis of 4-fluoro-1-butyl-*l*-d_2 trifluoromethanesulfonate.

Taking the value of k_s for each of the compounds listed in Table I as that value which lies on the line of Figure 1, and taking the value of k_Δ as the difference between the experimental rate constant and k_s, a ratio of k_Δ/k_s is obtained for each compound (Table III). These values also are listed in the form $100k_\Delta/(k_\Delta + k_s)$ for later comparison with the per cents of halogen-shifted products formed (also listed in Table III).

Table III. Calculated k_s, k_Δ, and k_Δ/k_s Ratios for Trifluoroacetolyses

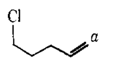
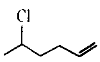
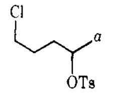
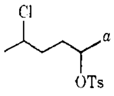
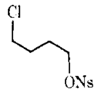
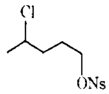
Nosylate	k_Δ/k_s	$100k_\Delta/(k_\Delta + k_s)$	Halogen shift, %
2-Chloro-1-propyl	~2000	99.95	99 ± 1
4-Chloro-1-pentyl	760	99.87	99.5
5-Chloro-1-hexyl	7.1	88	90
6-Chloro-1-heptyl	0.20[a]		17
4-Chloro-1-butyl	170	99.6	~50
5-Bromo-1-hexyl	25	96	93

[a] Distribution between k_s and k_Δ calculated from product data (see Table II) rather than from attenuation plots.

Turning to an examination of the rate data in Tables I and III we note (Table I) that our solvolyses of primary nosylates exhibit marked rate accelerations (up to 100-fold for 5-chloro-2-pentyl) owing to halogen participation, even when no allowance is made for inductive effects, in contrast with secondary tosylate solvolysis. However, the raw rate data do not reveal the striking preponderance of reaction *via* a three-membered chloronium ion that is indicated by the k_Δ/k_s value of 2000 (Table III). The rate data in Table III also show that the tendency for 1,4-chlorine participation (k_Δ/k_s = 760) is comparable to that for 1,2 participation,[11] and that 1,5-chlorine and bromine participation, although less favored, predominate over solvolysis without participation. The similarity of chlorine and bromine in their tendency for participation is also found for 1,4-participation reactions of haloalkynes[2] and alkenes.[12] The possible reasons for the striking contrast with the behavior in 1,2 participation have been discussed.[2]

Primary and secondary halogens as participating groups are compared in Table IV. The modest preference for participation of secondary halogen in various reactions presumably reflects the electron-releasing capability of alkyl substituents in the halonium ion intermediates. According to this postulate, halonium ions reflect in some degree the stability order of the corresponding carbonium ions.

Table IV. Relative Participation Tendency of Primary and Secondary Chlorides

Primary chlorides	k_Δ/k_s	Secondary chlorides	k_Δ/k_s
	8.6		11
	33		99,[b] 65[c]
	170		760

[a] Data from ref 5. [b] Erythro. [c] Threo.

The Nonhalogen Participation Reaction. We have arbitrarily chosen hexyl nosylate, not ethyl nosylate, as the unsubstituted compound whose rate of solvolysis is used in obtaining k_H/k_X ratios. Based on work from Winstein's group[13] it appears likely, however, that the rate constant for solvolysis of hexyl nosylate is itself a composite of rate constants for reactions involving hydrogen participation and solvent participation. In the cited study[13] it was shown that deuterium shift occurred in the trifluoroacetolysis of 1-propyl-*2,2*-d_2 tosylate to give approximately 90% secondary propyl trifluoroacetate.

If the per cent of secondary trifluoroacetates formed is a measure of hydrogen participation in the reactions of our study (as in the cited[13] study), the data of Table II show that 1-hexyl nosylate solvolyzes with 88% hydrogen participation. 5-Chloro-1-hexyl nosylate gives 7% of the product of hydrogen participation, **9**, along with 3% of "normal" primary trifluoroacetate **8**, in addition to previously mentioned products of halogen participation. Presumably the inductive substituent has decreased the extent of hydrogen participation compared to the values found for the 1-propyl or 1-hexyl systems. Since we have insufficient data to analyze k_s for other reactions by further separation into components, we give in Table V a conventional tabulation of inductive effects, involving comparison of the k_s value (also desig-

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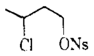
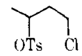
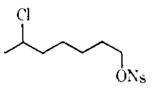
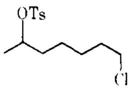
(10) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

(11) Chlorine participation was not evident in the well-known study of 2-halocyclohexyl brosylate acetolysis ((a) E. Grunwald, *J. Amer. Chem. Soc.*, **73**, 5458 (1951); (b) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948)) although evidence from formolysis and trifluoroacetolysis suggests that the acetolysis was a borderline case. (c) P. E. Peterson and J. E. Duddey, Ph.D. Thesis, St. Louis University, 1967.

(12) P. E. Peterson and G. Allen, *J. Amer. Chem. Soc.*, **85**, 3608 (1963).

(13) I. L. Reich, A. Diaz, and S. Winstein, *ibid.*, **91**, 5635 (1969).

Table V. ρ_I and ϵ Values in Trifluoroacetolyses

Primary nosylates	$\rho_I{}^a$	Secondary tosylates	$\rho_I{}^b$
	−4.04		−5.36
	-0.42^c		−1.25
ϵ, primary nosylates	0.46^d	ϵ, secondary tosylates	0.62

[a] Calculated from experimental values of log k_H/k_X using a chlorine σ_I value of 0.47. [b] Taken from ref 5. [c] Based on $k_x = k_{total} - k_\Delta = k_t - 0.17k_t$. [d] Based on least-squares slope, Figure 1; log $\epsilon = -0.3364$.

nated k_X) for substituted compounds with the experimental total rate constant for reaction of the unsubstituted compound, 1-hexyl tosylate. Although the unsubstituted compound would preferably be the one having the same chain length as the substituted one, previous work suggests that the rate would be insensitive to chain length for the series 1-propyl through 1-hexyl.[5] The reader may envision influences upon the ρ and ϵ values given in Table V which arise from ignoring hydrogen participation, but the values given do have the merit of being directly comparable to those previously given for secondary tosylates (*cf.* Table V). In the case of 3-chloro-1-butyl nosylate, the substantial ρ_I value would be moderately reduced by an allowance for hydrogen participation in the reference-unsubstituted nosylate, but substantial positive charge in the transition state of the normal reaction, involving substitution by solvent molecules, is nevertheless indicated.[14] On the other hand the normal acetolysis or formolysis reaction of a primary sulfonate[8] (or secondary sulfonate[5,14]) may be presumed to have considerable S_N2 character. Salt effects observed in the trifluoroacetolysis of ethyl tosylate support the ionic character of the transition state.[15]

Comparison of Rate and Product Studies. We note (Table III) that there is general agreement between the per cent of halogen participation based on analysis of rates and that based on the per cent of halogen-shifted products formed. Careful inspection of the data shows that the nearly quantitative participation tends to mask some appreciable differences in the two different estimates of the extent of the nonparticipation reaction. The two estimates are in agreement for the 5-halo-1-hexyl nosylates. However, our discussion of ambiguities involved in dealing with hydrogen participation tends to show that this agreement is fortuitously good. Nevertheless, the general success of predicting products from a careful analysis of reaction rates is comparable to that achieved in other recent studies, and some not so recent.[8,16] In general it may be said that the more accurate assessment of inductive effects in recent studies has led to a refinement of our ability to discern the extent of participation processes occurring in competition with other solvolytic processes.

Experimental Section

General. Glc analyses were made on flame ionization instruments made by F & M Scientific Corp. (Model 609) and Hewlett Packard Corp. (Model 5750). Nmr spectra were run on Varian Associates' Models A-60 and HA-100D, and, in all cases, were consistent with the original structure. Uv spectra were run on Bausch and Lomb's Model 505. Microanalyses were obtained from Galbraith Laboratories, Knoxville, Tenn., and Scandinavian Microanalytical Laboratories, Herlev, Denmark.

The following compounds were prepared by previously reported methods: 4-chloro-1-pentyl acetate,[16] 4-chloro-1-pentanol,[16] 5-hexen-2-ol,[17] 5-chloro-1-hexene,[17] 5-bromo-1-hexene,[18] 6-hepten-2-one,[16] 6-hepten-2-ol,[16] 6-chloro-1-hexene,[19] 6-chloro-3-hexanone,[20] 2-chloro-1-propanol,[21] and 3-chloro-1-butanol.[22]

6-Chloro-1-heptene. This compound was prepared from 6-hepten-2-ol, dissolved in an equimolar amount of pyridine, by reaction at 25° with an equimolar amount of thionyl chloride, followed by work-up with pentane and distillation through a spinning band column: yield, 7.0 g (35%); bp 69° (50 mm).

5-Chloro-1-hexanol. The compound was prepared from 5-chloro-1-hexene by hydroboration according to the procedure of Brown and Zweifel,[23] using 2-methyl-2-butene, freshly prepared by dehydration of *tert*-amyl alcohol, to prepare the borating agent. The amyl alcohol coproduct and diglyme solvent were removed by two-stage distillation through a spinning band column at 40 and 3 mm: yield, 13.1 g (64%); bp 81–82° (3 mm); nmr δ 1.50 (d, 3, CH_3CHCl-), 3.43 (t, 2, -CH_2OH), 4.00 (m, 1, -CHCl-).

Anal. Calcd for $C_6H_{13}OCl$: C, 52.74; H, 9.59. Found: C, 53.07; H, 9.93.

5-Bromo-1-hexanol. The compound was prepared from 5-bromo-1-hexene except that distillation was in three stages, 40, 3, and 0.8 mm: yield, 10.3 g (38%); bp 87–92° (0.8 mm); nmr δ 1.75 (d, 3, CH_3CHBr-), 3.63 (t, 2, -CH_2OH), 4.12 (m, 1, -CHBr-).

Anal. Calcd for $C_6H_{13}OBr$: C, 39.79; H, 7.23. Found: C, 39.55; H, 4.46.

6-Chloro-1-heptanol. Preparation was from 6-chloro-1-heptene using the procedure described for the preparation of 5-chloro-1-hexanol, except that distillation was in three stages, 40, 3, and 0.8 mm: yield of distillate (92% purity by glc), 2.2 g (37%); bp 75–78° (0.8 mm). Attempts to purify further by preparative glc (6-ft DC-550 column, 150°) were unsuccessful due to decomposition on the column: nmr δ 1.48 (d, 3, CH_3CHCl-), 3.52 (t, 2, -CH_2OH), 4.44 (m, 1, -CHCl-).

Anal. Calcd for $C_7H_{15}OCl$: C, 55.80; H, 10.04. Found: C, 56.47; H, 10.06.

4-Fluoro-1-butanol.[24] The compound was prepared by a three-step synthesis from ethyl 4-chlorobutyrate involving: (1) conversion to the iodobutyrate by halogen exchange with sodium iodide in acetone, (2) conversion to the fluorobutyrate by halogen exchange with potassium fluoride in ethylene glycol,[25] and (3) reduction with $LiAlH_4$ in ether solution:[26] yield, 1.2 g (3.5%); bp 56° (15 mm); nmr δ 3.56 (t, 2, -CH_2OH), 4.39 (d of t, 2, FCH_2CH$_2$-).

4-Chloro-1-butanol-*1-d*$_2$.[24] The compound was prepared from ethyl 4-chlorobutyrate by reduction with $LiAlD_4$ in ether solution: nmr δ 3.56 (no signal), 4.39 (d of t, 2, FCH_2CH$_2$-).

Nosylates. These were prepared from their alcohol precursors by reaction with an equimolar amount of recrystallized *p*-nitrobenzenesulfonyl chloride in pyridine solution, quenching in an excess of cold 6 *N* HCl solution, extraction with chloroform, and final recrystallization from ether–petroleum ether solution according to the procedure of Johnson and Owyang.[27] The primary compounds were stable to storage for as much as a year at 0°. Data pertaining to the compounds are given in Table VI.

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[27] W. S. Johnson and R. Owyang, *J. Amer. Chem. Soc.*, **86**, 5593 (1964).

Table VI. Data for Nosylates

Nosylate	Yield,[a] %	Uncorr mp, °C	Anal.			
			Calcd		Found	
			C	H	C	H
Ethyl	42	90.5–91.5				
Isopropyl	18	53–54				
1-Hexyl	48	51.5–52.5				
2-Chloro-1-propyl[b]	75[c]	79.0–81.2				
3-Chloro-1-butyl[b]	75[c]	54.1–57.2				
4-Chloro-1-pentyl	39	57.0–57.4	42.93	4.67	42.95	4.58
5-Chloro-1-hexyl	48	49.5–50.0	44.29	5.01	45.21	4.79
6-Chloro-1-heptyl	25	52–53	46.49	5.40	46.25	5.19
4-Chloro-1-butyl	28	61.5–62.0				
4-Chloro-1-butyl-1-d_2	40	60.6–61.0				
4-Fluoro-1-butyl	13	64.5				
5-Bromo-1-hexyl	27	51.0–51.5	39.35	4.40	39.55	4.46

[a] After recrystallization, except as noted otherwise. [b] Prepared by F. J. Slama. [c] Yield of chloroform evaporate.

Table VII. Data for Reference Trifluoroacetates

Trifluoroacetate	Yield, %	Bp, °C (P, mm)	Anal.			
			Calcd		Found	
			C	H	C	H
1-Hexyl	20	51 (15)				
2-Hexyl	66	42 (15)				
3-Hexyl	70	37–38 (15)				
4-Chloro-1-pentyl	67	68–70 (15)	38.46	4.61	38.54	4.79
5-Chloro-2-pentyl[a]	60	82 (61)				
5-Chloro-1-hexyl	62	80–81 (15)	41.30	5.20	41.59	5.24
5-Chloro-2-hexyl[b]						
6-Chloro-2-hexyl[c]	62	78 (10)	41.30	5.20	41.25	5.19
6-Chloro-3-hexyl[d]	(Recovd by preparative glc)		41.30	5.20	41.47	5.24

[a] Prepared by method given in ref 5. [b] Prepared by method given in ref 15. [c] Alcohol precursor prepared from 6-chloro-1-hexane by the oxymercuration–demercuration procedure of H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967): yield 2.0 g (37%); bp 78° (3 mm). [d] Alcohol precursor prepared from 6-chloro-3-hexanone by reduction in methanol solution with a basic water solution of sodium borohydride: yield of 85% purity distillate, 0.8 g (24%); bp 60–65° (5 mm).

Reference Trifluoroacetates. These compounds were prepared from their alcohol precursors in ether solution, except where indicated otherwise, by reaction with 1.20 mol of trifluoroacetic anhydride per mole of alcohol and working up by washing successively with water, saturated sodium chloride brine, saturated sodium bicarbonate solution, and saturated sodium chloride brine, drying with anhydrous magnesium sulfate, and distilling through a spinning band column. Data pertaining to these compounds are given in Table VII.

Trifluoroacetolysis Rate Method. A 0.003 M solution in redistilled trifluoroacetic acid, previously made 0.004 M in vacuum-dried sodium trifluoroacetate, was prepared by dissolving 0.075 mmol (17–25 mg) of the crystalline nosylate in the solvent and diluting to exactly 25 ml. Two-milliliter portions of this solution were immediately transferred to each of eight ampoules (made from 10-mm Pyrex glass tubing) contained in a Dewar flask and surrounded by crushed Dry Ice. After being filled, the ampoules were flushed with dry nitrogen, sealed, and totally immersed in a 60.0° water bath.

Samples were taken at zero time and at intervals of one-fifth of the estimated half-life by withdrawing an ampoule, cooling it in cold tap water, breaking it open, and withdrawing exactly 1.00 ml with a pipet. The pipet contents were then quenched by injecting immediately into 99.5% isopropyl alcohol (made by adding 0.5 ml of water to 100 ml of spectroscopic grade isopropyl alcohol) contained in a 50-ml volumetric flask. The solution was diluted to the mark with additional 99.5% isopropyl alcohol, and the uv spectrum was run over the range of 245–350 mμ using, as reference, a solution of 1.00 ml of the solvolysis solvent similarly diluted to 50 ml with 99.5% isopropyl alcohol.

The rate of solvolysis was evaluated by graphing the natural logarithm of the difference between the absorbance of each sample and the absorbance at complete solvolysis, both at 275 mμ, *vs.* the time at which the sample was taken. (Absorbance at complete solvolysis was determined experimentally for each nosylate with a half-life of 50 hr or less and was estimated from the extinction coefficient of the anion for the others.) The first-order rate constant was taken as the negative of the slope of the least-squares straight line through the points. All the operations involved, including graphing, were handled by computer. The data were culled before feeding to the computer by eliminating any points based on spectra which did not pass through the isosbestic point or which represented samples taken past two half-lives.

Satisfactory straight lines were obtained for all compounds except 2-chloro-1-propyl nosylate. In this case, where the points actually defined an accelerating curve, the rate constant was taken as that prevailing during the initial reaction.

The computer-calculated 95% confidence limits of the rate constants were all in the ±3 to ±17% range, except those for 3-chloro-1-butyl nosylate. For this compound a range of ±28% was encountered due to terminating the run at 40% of the half-life.

Preparative Scale Solvolyses. The following procedure was used for the trifluoroacetolysis of **2-chloro-1-propyl nosylate**, for the acetolysis, formolysis, and trifluoroacetolysis of **4-chloro-1-pentyl nosylate**, and for the trifluoroacetolysis of **5-chloro-1-hexyl nosylate**.

A 0.175–0.350 M solution was made by dissolving 6.4–10.8 g (0.020–0.035 mol) of the crystalline nosylate in the appropriate acid contained in a 100- or 200-ml volumetric flask, adding either no buffer or a 14% excess of vacuum-dried sodium salt of the acid, and diluting to the mark at the reaction temperature. Reaction was carried out by immersing to the liquid level in a 60.0 or 70.0° thermostatic bath. Work-up was similar to that described for the preparation of the reference trifluoroacetates. Yields are given in Table VIII.

Nmr spectra of the recovered distilled products showed prominent three-proton doublets at δ 1.50 (CH_3CHCl–) and at 1.20 (CH_3CHOAc–), 1.25 (CH_3CHOCOH–), or 1.35 (CH_3CH-OCOCF$_3$–), together with other features characteristic of the products of normal and halogen-shift solvolyses. No products other than these were discernible from the nmr spectra.

The degree of halogen shift was estimated from the integrals of the above mentioned methyl doublets at δ 1.50 (unshifted halogen) and at 1.20, 1.25, or 1.35 (esters from halogen shift), reinforced, in the case of the trifluoroacetolyses of 2-chloro-1-propyl, 4-chloro-1-pentyl, and 5-chloro-1-hexyl nosylates, by glc analyses of the products.

Table VIII. Data for Preparative Scale Solvolyses

Nosylate	Solvent	Distillate yield, %	Pot residue yield, %
2-Chloro-1-propyl[a]	$CF_3COOH-NaOCOCF_3$		
4-Chloro-1-pentyl	HOAc–NaOAC	65	1.1
4-Chloro-1-pentyl	HOAc	66	0.8
4-Chloro-1-pentyl	HCOOH–NaOCOH	54	0.6
4-Chloro-1-pentyl	$CF_3COOH-NaOCOCF_3$	57	4.9
5-Chloro-1-hexyl	$CF_3COOH-NaOCOCF_3$	42	23

[a] Carried out by F. J. Slama.

The identification of the two major products from 5-chloro-1-hexyl nosylate was confirmed by collecting the compounds contained in each peak separately by preparative gas chromatography (6-ft DC-550 column, 120°) and comparing the nmr spectra of the collected material with those of authentic samples. The spectra were identical.

Sealed Tube Solvolyses. An approximately 0.1 *M* (**1-hexyl** and **5-bromo-1-hexyl nosylates**) or 0.4 *M* (**6-chloro-1-heptyl nosylate**) buffered solution was prepared by weighing out the appropriate quantity of crystalline nosylate, together with a 25–50% *M* excess of vacuum-dried sodium trifluoroacetate, into a Dry Ice chilled ampoule or nmr tube, adding the appropriate quantity of redistilled trifluoroacetic acid by pipet, flushing with dry nitrogen, and sealing. The container was then totally immersed in a 60.0° water bath for 7–8 half-lives (1-hexyl and 5-bromo-1-hexyl nosylates) or 1.8 half-lives (6-chloro-1-heptyl nosylate). Subsequent product work-up and analysis varied with the compound as follows.

For **1-hexyl nosylate** the products were worked up quantitatively into a dry ether solution (by the method used for the reference trifluoroacetates) and analyzed by glc (4.0 μl injections, 6-ft TCEP column with 8-in. base forecolumn,[28] programmed temperature of 70–100°). The product composition and yield (96%) were determined by comparison of the resulting chromatogram with chromatograms of the products from an identical work-up of an authentic mixture of 1-hexyl, 2-hexyl, and 3-hexyl trifluoroacetates.

For **5-bromo-1-hexyl nosylate** the reaction mixture was evaporated to one-quarter its original volume and an nmr spectrum was taken. Relative amounts of primary and secondary bromides were estimated by comparing the integral at δ 3.43 (t, $-CH_2Br$) with twice the integral at 4.02 (m, $-CHBr-$). The relative amounts of primary and secondary trifluoroacetates were estimated in a similar manner using the integrals at δ 4.50 (t, $-CH_2OCOCF_3$) and 5.20 (m, $-CH-OCOCF_3-$). The relative amounts of 6-bromo-2-hexyl and 6-bromo-3-hexyl trifluoroacetates were estimated from the integrals at δ 1.44 (d, CH_3CHBr-) and 1.00 (t, CH_3CH_2Br-).

For **6-chloro-1-heptyl nosylate** an nmr spectrum was taken on the contents of the still-sealed tube, using an external TMS capillary as reference. (Peaks were observed having δ values 1–2, 3.59 (t, primary chloride), 4.05 (secondary chloride), 4.35 (t, unreacted nosylate), 4.52 (t, primary trifluoroacetate), and 5.27 (secondary trifluoroacetate)). The relative areas were divided by 1, 2, or 11 (peak at δ 1–2) depending on the number of hydrogens contributing to the peak, to obtain the relative molarities 13.6, 2.35, 7.75, 1.25, 3, and 4.5, respectively. Compounds differing from **6**, **7**, **8**, and **9** (this paper) only by the presence of an additional methylene group may be envisioned as the sources of these signals. The areas do not show full internal consistency, but the ratio of primary chlorides to all compounds, 2.35/13.6 = 0.173, should be relatively free of interference due to unanticipated components. (The presence of 12, not 11, upfield hydrogens in compounds analogous to **9** is not a serious problem.)

Trifluoroacetolysis of 4-Chloro-1-butyl-*1*-d_2 Nosylate.[29] An approximate 0.1 *M* buffered solution of the nosylate in redistilled trifluoroacetic acid containing a molar excess of vacuum-dried sodium trifluoroacetate was prepared and allowed to react for 15 half-lives at 60.0°. A time-averaged nmr spectrum of the reacted mixture indicated complete scrambling of the deuterium in the products as evidenced by identical integrals of the proton signals at δ 3.59 (t, $-CH_2Cl$) and 4.50 (t, $-CH_2OCOCF_3$). A time-averaged spectrum taken at 0.5 half-life indicated no scrambling of the deuterium in the nosylate as evidenced by the absence of any signal at δ 4.37 (t, $-CH_2ONs$).

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N,N'-Dimethylcarbodiimide, Pure Monomer. II. Spectroscopic Properties[1,2]

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Abstract: The main spectroscopic properties of *N,N'*-dimethylcarbodiimide have been investigated. Infrared spectra from 4000 to 200 cm^{-1} of gaseous, liquid, and solid samples as well as the Raman spectrum of the liquid were measured and a detailed vibrational assignment was reported. Uv and nmr spectra were examined and discussed. The combined analysis of the spectroscopic data supports a low molecular symmetry structure (C_2 point group) and shows the existence of close analogies with the allene-type compounds.

The problem of the molecular structure of symmetrically substituted carbodiimides has been previously discussed by several authors. Only recently a structure like that of allenes has been proved on the basis of the following results: (i) isolation of the optically active *N,N'*-diferrocenylcarbodiimide; this implies a low symmetry structure of the molecule;[3] (ii) dipole mo-

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