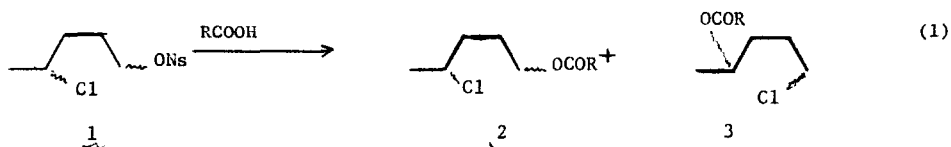


1,4-AND 1,5-HALOGEN SHIFTS  
IN THE SOLVOLYSIS OF PRIMARY NOSYLATES

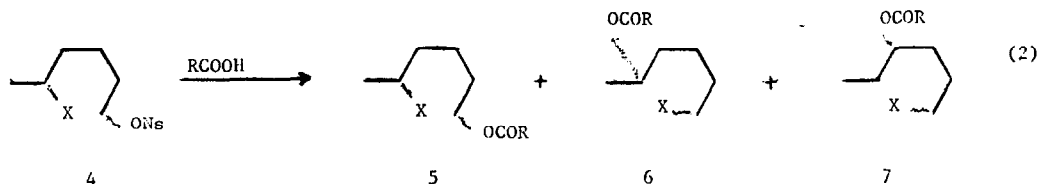
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We wish to report that the trifluoroacetolysis of the primary p-nitrobenzenesulfonate (nosylate), 1, leads cleanly and almost exclusively (to the extent of 99.5%) to the product of 1,4-chlorine shift (eq. 1, product 3).



In similar reactions we have found the first examples of 1,5-halogen shifts in carbonium ion reactions (eq. 2).



In the latter reaction 5-halo-1-hexyl nosylate gave the normal solvolysis product 5, in addition to halogen shifted products, (the expected one, 6, and the rearranged one, 7) and some polymer.

Previously examples of 1,4-halogen shifts have been noted in cationic reactions of alkenes, alkynes and secondary tosylates.<sup>1,2,3,4</sup> The greatly enhanced participation effects exhibited in the trifluoroacetolysis of the primary sulfonate (eq. 1) are reflected also in the reaction rate, which is approximately 500 times that of ethyl nosylate. Secondary tosylates<sup>4</sup> showed marked enhancements only after correction for inductive effects.

The marked ability of trifluoroacetic acid to promote reaction via a participation pathway is emphasized in Table I in which data for solvolyses in other carboxylic acid solvents is included.

TABLE I  
SOLVOLYSES OF PRIMARY ALKYL NOSYLATES

<u>Substrate</u>	<u>Solvent</u>	<u>Temperature</u>	<u>Reaction Time, Hours</u>	<u>Halogen Shift, %<sup>a</sup></u>
4-Chloro-1-pentyl	HOAc-NaOAc	70°	148	5
" " " "	HOAc	70°	360	27
" " " "	HCOOH-NaOCOH	60°	69	60
" " " "	HCOOH	60°	75	67 <sup>b</sup>
" " " "	CF <sub>3</sub> COOH-NaOCOCF <sub>3</sub>	25°	167	99.5
5-Chloro-1-hexyl	CF <sub>3</sub> COOH-NaOCOCF <sub>3</sub>	60°	168	93
5-Bromo-1-hexyl	CF <sub>3</sub> COOH	60°	60	95+ <sup>b</sup>

(a) Estimated, except as noted, from the n.m.r. spectra (neat liquid) of the distilled solvolysis product, reinforced, in the case of the 99.5% shift, by capillary glc analysis. (b) Estimated from the n.m.r. spectrum of the concentrated, undistilled reaction product.

Very recently, a similar solvent influence upon the occurrence of 1,2-phenyl participation<sup>5</sup> and triple bond participation<sup>6</sup> in primary sulfonate solvolyses has been observed. The incursion of an S<sub>N</sub>2 path in the reaction of 1 when sodium acetate or sodium formate is included in the solvent is interestingly reflected (Table I) as a marked decrease in the percent of halogen shift.

We note finally that the use of nosylates was particularly advantageous in that they were recrystallizable solids which reacted faster and somewhat more cleanly than tosylates.

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