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New Synthetic Techniques for Advanced Propellant Ingredients:

Trifluoromethanesulfonate Derivitive Intermediates

April 1987

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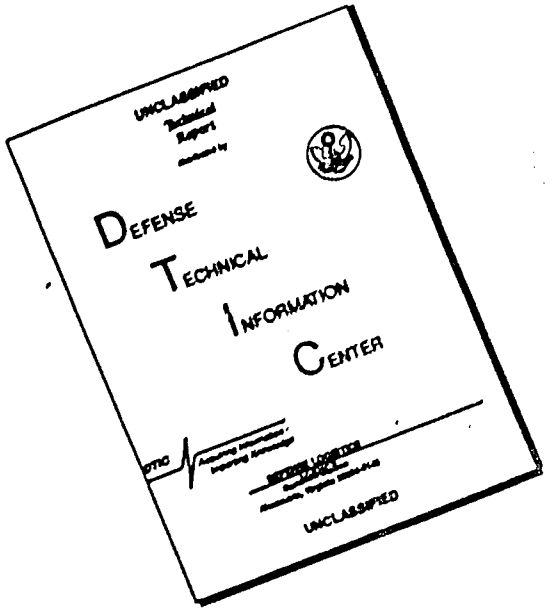

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FOREWORD

This final report describes an advanced propellant ingredient synthetic techniques study performed at the Air Force Astronautics Laboratory (AFAL), Edwards Air Force Base, CA. AFAL Project Manager was Bob Chapman.

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The metathesis reaction between silver triflate and bromoalkanes potentially offers an attractive synthetic complement to the well known alcohol condensation with triflic anhydride for organic triflate esters. Dibromoalkanes can further give difunctional triflate intermediates and could provide convenient routes to asymmetrically substituted derivatives. Certain shorter members of the α,ω-dibromoalkane homologous series display a unique reactivity and product selectivity over higher homologues and corresponding 1° monobromoalkanes. Triflate products from monobromoalkanes and α,ω-dibromoalkanes greater than 1,4-dibromobutane can lead to benzene solvent alkylation or polymerization in CCl_4, but the lower 1,2- through 1,4-dibromoalkanes produce desired monobromoalkyl triflate and alkanediyl ditriflate products under the same reaction conditions. These same lower α,ω-dibromoalkanes also resist product rearrangement to 2° triflate products while the higher homologous α,ω-dibromoalkanes and

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19. 1° monobromoalkanes do not. The 1,2- through 1,4-dibromoalkanes further offer selective synthesis routes to difunctional derivatives via sequential metathesis. The unique stability and selectivity of the lower α,ω-dibromoalkane homologues are apparently best explained with anchimeric assistance by a cyclic bromonium ion in the first metathesis step followed by a rare example of cyclic anchimeric stabilization by the triflate group in the second bromine displacement. Kinetic results further support this mechanism. This metathesis reaction is, however, very dependent upon the control of several reaction conditions: dibromoalkane chain length, solvent, temperature, reaction time, and type of bromine leaving group. The optimum conditions for obtaining certain α,ω-alkanediyl ditriflates, ω-bromoalkyl triflates, and 1-butyl triflate are presented.

Metatheses between bromoalkanes and silver trifluoromethanesulfonate are generally facile under some reaction conditions, and the resulting triflate esters are useful as intermediates for the substitution of a variety of nucleophiles, even relatively poor ones such as polynitroaliphatic alcohols. However, the displacement in 1-bromo-2-(2-fluoro-2,2-dinitroethoxy)propane could not be effected because of the electronegative alkoxide's inductive effect. The scope of the utility of nucleophilic substitutions via this route involves other homologous α,ψ-dibromoalkanes [1,(n-1)-dibromoalkanes] and another vicinal dibromoalkane (2,3-dibromobutane), from which a variety of new fluorodinitroethyl ethers were made. The α,ψ-dibromoalkanes show a solvent dependence of mechanisms in reactions with silver triflate: anchimeric assistance by α-bromide occurs in carbon tetrachloride but not in benzene. Also, 1,3-dibromoalkanes are distinct among dibromoalkanes in showing a reaction rate of the second bromide's displacement which is comparable to or greater than that of the first step. Other α,ψ- and α,ω-dibromoalkanes are typically distinctly stepwise in their two possible S_N1Ag^+ displacements of bromide by silver triflate, a characteristic which allows selective incorporation of non-nucleophilic alkoxy substituents via displacements of triflate intermediates.

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Trifluoromethanesulfonate Esters from Dibromoalkane Metatheses with Silver Triflate: Mechanistic and Synthetic Aspects[1]

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The metathesis reaction between silver triflate and bromoalkanes potentially offers an attractive synthetic complement to the well-known alcohol condensation with triflic anhydride for organic triflate esters. Dibromoalkanes can further give difunctional triflate intermediates and could provide convenient routes to asymmetrically substituted derivatives. Certain shorter members of the α,ω-dibromoalkane homologous series display a unique reactivity and product selectivity over higher homologues and corresponding primary monobromoalkanes. Triflate products from monobromoalkanes and α,ω-dibromoalkanes greater than 1,4-dibromobutane can lead to benzene solvent alkylation or polymerization in CCl_4, but the lower 1,2- through 1,4-dibromoalkanes produce desired monobromoalkyl triflate and alkanediyl ditriflate products under the same reaction conditions. These same lower α,ω-dibromoalkanes also resist product rearrangement to secondary triflate products while the higher homologous α,ω-dibromoalkanes and primary monobromoalkanes do not. The 1,2- through 1,4-dibromoalkanes further offer selective synthesis routes to difunctional derivatives via sequential metathesis. The unique stability and selectivity of the lower α,ω-dibromoalkane homologues are apparently best explained with anchimeric assistance by a cyclic bromonium ion in the first metathesis step followed by a rare example of cyclic anchimeric stabilization by the triflate group in the second bromine displacement. Kinetic results further support this mechanism. This metathesis reaction is, however, very dependent upon the control of several reaction conditions: dibromoalkane chain length, solvent, temperature, reaction time, and type of bromine leaving group. The optimum conditions for obtaining certain α,ω-alkanediyl ditriflates, ω-bromoalkyl triflates, and 1-butyl triflate are presented.

High-yield organic trifluoromethanesulfonate (triflate) ester syntheses are normally accomplished by reacting the corresponding alcohol with triflic anhydride;[3-7] however, a few esters have been made by a complementary metathesis reaction between an alkyl halide and a metallic triflate salt.[4,5,8,9] One study has compared the metathesis reaction of primary monoiodoalkanes with silver triflate and silver perchlorate reagents;[6] but systematic investigation of this potentially useful methathesis approach as a synthetic alternative has not been reported. A preliminary report[10] of the metathesis reactions between dibromoalkanes and silver triflate reagent first hinted at such a potential synthetic selectivity by revealing a unique reactivity of certain α,ω-dibromoalkanes compared to higher dibromoalkane homologues and monobromoalkanes. Lower homologous α,ω-dibromoalkanes through 1,4-dibromobutane were stable with respect to subsequent alkylation of benzene solvent by their triflate intermediates or to polymerization in CCl_4; triflic acid was a catalytic byproduct in each case. These same dibromoalkanes did not rearrange to secondary triflate ester intermediates in CCl_4. A cyclic, albeit unconfirmed, anchimeric stabilization by the triflate group was proposed as being the most logical explanation.[10] The reaction parameters of temperature, time, solvent, and position and type of bromine atom were identified as parameters requiring further study in order to use this metathesis as an effective synthetic reaction. This research additionally identifies silver triflate purity and solvent stability as key parameters and quantifies the influence of each reaction parameter upon the desired monobromoalkyl triflate or alkanediyl ditriflate product yields noted in earlier reports.[10,11] The metathesis reaction of dibromoalkanes with silver triflate is strongly dependent upon controlling the interacting reaction parameters noted above and understanding the reaction mechanism's dependence upon the reactant's chemical structure. This study quantifies the influence of these reaction parameters and can serve as the first step for identifying and controlling necessary reactions with bromoalkanes not specifically addressed. In doing so, we demonstrate the potential of the alkyl bromide/silver triflate reaction system as a viable and flexible general synthetic technique.

Results and Discussion

The metathesis reaction between dibromoalkanes and silver triflate complements the better known alcohol condensation[3,7] in several ways. First, the bromoalkane precursor can be used when the reactant alcohol is not available. Second, it permits use of the storable solid

(1) Presented in part at the 189th National Meeting of the American Chemical Society, Miami Beach, FL, April 1985 (ORGN 254), and the 11th International Symposium on Fluorine Chemistry, East Berlin, Germany, Oct 1985 (C-13).

(2) Research conducted at both FJSRL (1975–1977) and AFRPL (1980–1984).

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Table I. Chain Length and Temperature Effects on α,ω-Dibromoalkane–Silver Triflate Reaction Compositions in Benzene Solvent[a]

	% $Br(CH_2)_nBr$:$Br(CH_2)_nOTf$:$TfO(CH_2)_nOTf$[b]	
n	54 °C	80 °C
2	46:54:0	0:88:12
3	14:67:19	0:24:76
4	0:42:58	0:0:100[c]
5	0:35:65[c]	dec
6	0:46:54[c]	dec
10	0:43:57[d]	dec

[a] Conditions: 1.75 mmol of dibromoalkane + 3.50 mmol of silver triflate in 5.00 mL of benzene, reaction time 20 h. [b] Percentages listed are mean values of several runs. Standard deviations of the mean estimates are 1–3 absolute %. [c] Partial decomposition. [d] Optimum composition after 11 h; extensive decomposition occurred by 20 h.

reagent, silver triflate, whereas triflic anhydride's hydrolytic instability and reactivity require greater experimental precautions. Third, the condensation approach sometimes cannot be used when a structural moiety is susceptible to triflic anhydride attack; in such cases, the silver triflate reagent can be used. One example recently encountered is epibromohydrin. Use of epibromohydrin's alcohol analogue, glycidol, is precluded by triflic anhydride attack on the oxirane ring,[12] but epibromohydrin reacts with silver triflate to produce the desired 2,3-epoxypropyl triflate.[13] Finally, this metathesis permits selective, stepwise formation of monobromoalkyl triflates from the lower homologous α,ω-dibromoalkanes. This could be useful for syntheses of asymmetric diethers or other difunctional derivatives. This appears especially feasible with dibromoalkanes containing different types of bromine sites.[10]

The highly labile nature of the triflate group makes it useful as a synthetic intermediate but also makes it very sensitive to reactant chemical structure, solvent characteristics, and extrinsic reaction conditions. These reaction parameters were investigated and quantified to assure this metathesis approach's validity as a general synthetic tool.

α,ω-Dibromoalkane Chain Length. Reactant chain length and the resultant bromine atom separation in the homologous α,ω-dibromoalkane series greatly affect the extent of triflate substitution. Reactions were initially carried out in benzene solvent with a 2:1 silver triflate to dibromoalkane stoichiometry at reflux temperature. Table I illustrates the extent of desired mono- or ditriflate product formation after 20-h reaction time. The ditriflate product formation increases from 1,2-dibromoethane to 1,4-dibromobutane, a trend that apparently results from the deactivating nature of the electronegative bromine and triflate substituents. Indeed, this effect is so strong in this homologous series that *no* triflate substitution occurs in the primary geminal dibromide, dibromomethane. With 1,2-dibromoethane, the first triflate substituent permitted only 12% of the bromoethyl triflate intermediate to form ditriflate because of this deactivation effect.[14] The olefin analogue, 1,2-dibromoethene, is likely enhanced further by the stronger sp^2-hybridized vinylic C–Br bond. Dibromoalkane homologues higher than 1,4-dibromobutane decomposed in refluxing benzene via solvent alkylation and optimum ditriflate conversion as a function of alkyl chain length and bromine atom separation could not be determined. However, at 54 °C, the alkylation problem is alleviated, so 1,5-dibromopentane, 1,6-dibromohexane, and 1,10-dibromodecane were investigated. Refluxing acetone in an outer-jacketed flask assured a constant reaction temperature and revealed that the trend toward greater ditriflate product yield essentially levels out at 1,4-dibromobutane, with a slight peaking at 1,5-dibromopentane.

Proton and ^{19}F NMR analyses of reaction aliquots revealed another feature dependent upon bromine separation. Metathesis steps with 1,4-dibromobutane occur via a stepwise sequence in benzene or CCl_4 solvent; 1,2-dibromoethane is stepwise up to 92% conversion to 2-bromoethyl triflate in the first step. The reaction steps of 1,3-dibromopropane overlap significantly more; a maximum of 66% of 3-bromopropyl triflate forms before the second step begins. Kinetic data in Table II provide useful information for monobromoalkyl triflate synthesis when *asymmetric difunctional* products are desired. With 1,6-dibromohexane, however, monotriflate and ditriflate formation is neither stepwise nor resolvable by ^{19}F NMR; this precluded accurate composition determinations. This same behavior continues with the 1,10-dibromodecane, although the relative concentration of total alkyl triflate products and total bromoalkanes can be determined by ^1H NMR from the corresponding methylene triplets. Optimum triflate formation at 54 °C in benzene occurs at ca. 11 h for the higher 1,6- and 1,10-dibromoalkane homologues when the $[RCH_2OTf]/[RCH_2Br]$ ratio equals 3.6 and a negligible amount of dibromoalkane reactant remains. Beyond the 1,4- or 1,5-dibromoalkane homologue, each end of the molecule functions as if it were a separate monobromoalkane. The higher stability of triflate products from 1,4-dibromobutane in refluxing benzene, the sharp leveling off of increasing ditriflate formation, and the disappearance of stepwise metathesis after 1,4-dibromobutane in the α,ω-dibromoalkane homologous series all point to an intramolecular dependence expected from anchimeric bridging mechanisms.

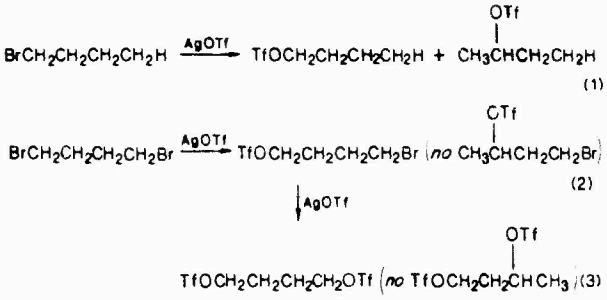
Carbon tetrachloride solvent provided a similar trend in the two-carbon through four-carbon homologues; however, the conversion to ditriflate product was much lower than with benzene. Conversion of $Br(CH_2)_3Br$ to ditriflate after 20 h was only 34% in refluxing CCl_4, but 76% in refluxing benzene. At 20 h, the products from 1,4-dibromobutane underwent polymerization. While CCl_4 can conveniently provide monobromoalkyl triflates below the 76 °C reflux, it has other disadvantages.

Solvent Effects. Benzene provides a better one-step ditriflate synthesis than CCl_4, and except for the first three α,ω-dibromoalkanes beginning with 1,2-dibromoethane, CCl_4 permits product rearrangement from all bromoalkanes to secondary triflate products. Product rearrangement from 1-iodopropane plus silver triflate at room temperature produced only 34% of the primary 1-propyl triflate and 66% of the rearranged secondary 2-propyl triflate.[15] A similar rearrangement occurs with 1-bromobutane and 1-bromopropane. The room-temperature reaction of 1-bromopropane affords 71% of rearranged 2-propyl triflate, while 1-bromobutane provides 60 ± 10% 2-butyl triflate plus the unrearranged 1-butyl triflate (eq 1).[16] No such product rearrangement occurs in benzene at any temperature. Surprisingly, the lower α,ω-dibromoalkanes display an unexpected stability against product

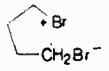
(12) Epoxide ring opening occurs with the convenient oxide and triflic anhydride. Shackelford, S. A. Avram, W. A. unpublished results.

(13) Taylor, M. A. [illegible] R. D. Andreshak, J. L. 1985 Pacific Conference on Chemistry and Spectroscopy, San Francisco, CA, Oct 1985; p 90. Yields from this reaction have not been optimized.

(14) [illegible] derivative can be effected in benzene or bromobenzene at still higher temperatures in pressure vessels. Hildreth, R. A. Fryling, J. A. unpublished results.



rearrangement. In CCl_4 at room temperature, 1,4-dibromobutane produced only the primary 4-bromobutyl triflate (eq 2) followed stepwise by the formation of unrearranged 1,4-butanediyl ditriflate (eq 3). Unrearranged monobromobutyl triflate (eq 2) is readily explained by intramolecular bromonium ion bridging and a resulting anchimeric assistance in displacing the first bromine substituent. The reaction rate shows a significant acceleration with 1,4-dibromobutane; $t_{1/2}$ = 0.95 h in this first metathesis step (eq 2), compared to 76.5 h for 1-bromobutane (eq 1); this strongly suggests neighboring group participation as shown in species **1**. The relative reaction



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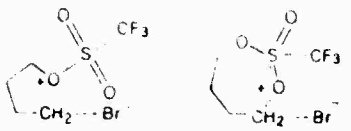
rates of 1,4-dibromobutane and 1,5-dibromopentane are 33:1 in room-temperature CCl_4 solvent, while those of CCl_4 reflux reactions of 1,2-dibromoethane, 1,3-dibromopropane, and 1,4-dihromobutane are 1:1.4:>28. Clearly, the 1,4-dibromoalkane homologue's significant rate enhancement further supports formation of the highly favored 5-membered cyclic bromonium ion. As shown in Scheme I, species **1** obviates the need for rearrangement to a more stable secondary ionic species via a 1,2-hydride shift. Anchimeric assistance by bridged alkylhalonium ions of this type is well documented.[15-17] Kinetic studies of this first displacement step (Table II) show that α,ω-dibromoalkanes react autocatalytically in CCl_4 or benzene, following the rate expression $-d[A]/dt = k[A][B]$ for the generalized reaction A → B.[18] Their susceptibility to heterogeneous autocatalysis in silver ion assisted carbon-halogen bond cleavage is a recognized mechanistic phenomenon.[19] In contrast, monobromoalkanes follow pseudo-first-order kinetics in CCl_4 solvent, in which AgOTf has a low solubility; in benzene, in which it is soluble, a 2.5-order rate law is followed such as that reported for 1- and 2-bromooctane reactions with $AgNO_3$.[20]

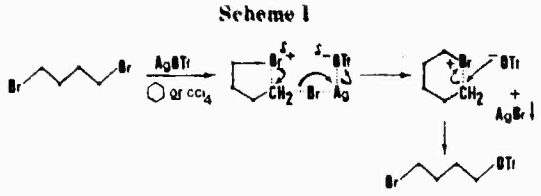
The lack of product rearrangement in the second displacement by triflate (eq 3) is especially noteworthy. Like the 1-bromobutane (eq 1), the 4-bromo-1-butyl triflate (eq 2) has no bromine to provide the cyclic bromonium ion stabilization at the primary attack site, which would eliminate the need for rearrangement to the more stable secondary carbonium ion species. Substantial rearrangement via a 1,2-hydride shift would be expected. This lack of rearrangement is best explained by the rare formation of a bridging triflate group (**2** or **3**) in the reaction illus-



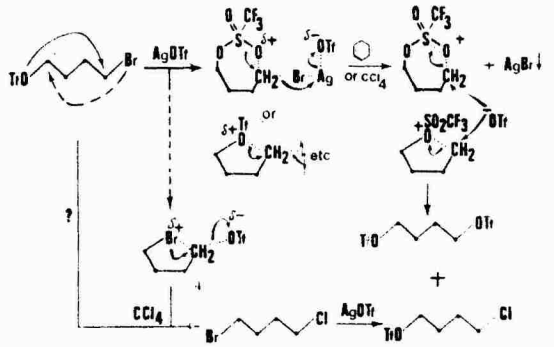
2 **3**

trated by Scheme II (top). Anchimeric assistance by the triflate group is reported in organosilicon triflate solvolyses,[21] and our results further verify the triflate group's potential for intramolecular anchimeric bridging when reaction conditions permit or require it. We propose the more traditional acetoxonium[17,22] analogue **3** for this likely triflate anchimeric stabilization, but possible contributions from **2** cannot be ruled out. Introduction of the first triflate group deactivates the *n*-butyl skeleton; the 267-h reaction half-time (eq 3) is 3.5 times longer than that of eq 1. Triflate group anchimeric stabilization ends with 1,4-dibromobutane; the higher 1,5- and 1,6-dibromoalkane homologues produce rearranged secondary triflate products (~40%) in CCl_4 as monitored by ^1H NMR. Still, rear-

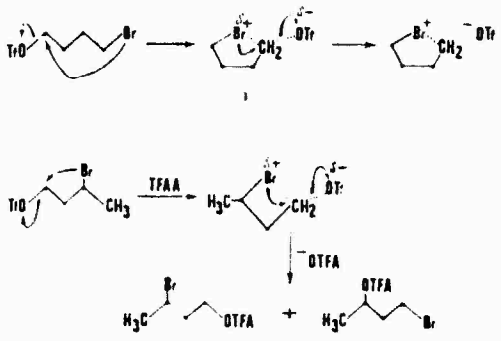
Scheme I



Scheme II



Scheme III[a]



[a] Bottom: Peterson, P. E.; Coffey, W. F. *J. Am. Chem. Soc.* 1971, *93*, 4076.

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Table II. Kinetic Parameters of Silver Triflate–(Di)Bromoalkane Reactions[a]

solvent	temp, °C	bromoalkane reactant	behavior (rate law)	rate const, k
CCl_4	room temp	$CH_3CH_2CH_2CH_2Br$	pseudo first order	2.52×10^{-6} s^{-1}
		$Br(CH_2)_4Br$	autocatalytic	5.41×10^{-3} M^{-1} s^{-1}
		$Br(CH_2)_4OTf$	pseudo first order	7.20×10^{-7} s^{-1}
		$Br(CH_2)_5Br$	autocatalytic	1.61×10^{-4} M^{-1} s^{-1}
CCl_4	reflux	$Br(CH_2)_2Br$	autocatalytic	1.81×10^{-3} M^{-1} s^{-1}
		$Br(CH_2)_3Br$	autocatalytic	2.48×10^{-3} M^{-1} s^{-1} [b]
		$CH_3CH_2CH_2CH_2Br$	pseudo first order	1.27×10^{-3} s^{-1}
		$Br(CH_2)_4Br$	autocatalytic[c]	$>50 \times 10^{-3}$ M^{-1} s^{-1}
		$Br(CH_2)_4OTf$	pseudo first order	9.96×10^{-5} s^{-1}
C_6H_6	54	$CH_3CH_2CH_2CH_2Br$	2.5 order	4.04×10^{-4} $M^{-1.5}$ s^{-1}
		$Br(CH_2)_5Br$	autocatalytic	2.13×10^{-3} M^{-1} s^{-1}
		$Br(CH_2)_6Br$	autocatalytic	3.76×10^{-3} M^{-1} s^{-1}
		$Br(CH_2)_{10}Br$	autocatalytic	3.96×10^{-3} M^{-1} s^{-1}
C_6H_6	reflux	$Br(CH_2)_2Br$	autocatalytic	4.34×10^{-4} M^{-1} s^{-1} [b]
		$Br(CH_2)_2OTf$	2.5 order	7.95×10^{-4} $M^{-1.5}$ s^{-1}
		$Br(CH_2)_3OTf$	2.5 order	2.20×10^{-4} $M^{-1.5}$ s^{-1}
		$CH_3CH_2CH_2CH_2Br$	2.5 order	1.83×10^{-3} $M^{-1.5}$ s^{-1}
		$Br(CH_2)_4Br$	autocatalytic[c]	$>1 \times 10^{-1}$ M^{-1} s^{-1}
		$Br(CH_2)_4OTf$	2.5 order	9.14×10^{-4} $M^{-1.5}$ s^{-1}

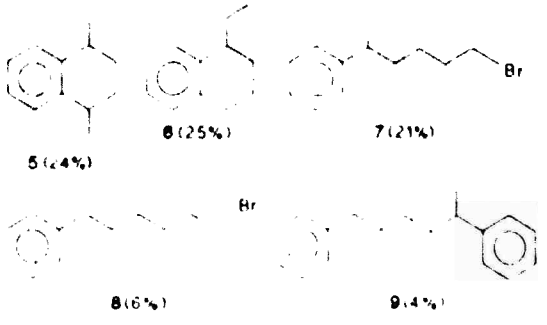
[a] Reaction scale: 1.75 mmol of (di)bromoalkane + 1.75 mmol of AgOTf (for monobromoalkane) or 3.50 mmol of AgOTf (for dibromoalkane) in 5 mL of solvent. [b] Concurrent steps during part of reaction course. [c] Presumed, not measured.

rangement is less than in monobromoalkanes (~70%).

This apparent anchimeric assistance is permitted by silver ion complexation in the second metathesis step (Scheme II, top). If displacement of the second bromine leaving group were not assisted by silver complexation, an alternative reaction could occur wherein the labile triflate group would be attacked via a cyclic halonium ion (Schemes II and III, top), for which there is literature precedence (Scheme III, bottom).[15] This competing mechanism apparently occurs to some extent. By ^{13}C NMR, we identified a minor reaction product, 4-chlorobutyl triflate (confirmed by an independent synthesis), in one reaction system. The uncomplexed bromine must generate a bromonium anchimer, **4** (Schemes II and III), which assists in displacing the nonbridging triflate group with a chlorine species provided by the CCl_4 solvent to form a 1-bromo-4-chlorobutane intermediate. Displacement of the more labile bromine by silver triflate in a subsequent reaction would produce 4-chlorobutyl triflate. Although CCl_4 solvent can provide a high-yield, one-step metathesis when conducted under mild reaction conditions, it is not stable to high-temperature reaction conditions. CCl_4 solvent allows faster reactions than benzene at comparable temperatures,[8] but it also reacts with the silver triflate reagent itself. This reaction and an analogous metathesis of mercury(II) triflate with CCl_4 form trichloromethyl triflate (CCl_3OTf).[23] We have observed this solvent derivative in all dibromoalkane/silver triflate product solutions in refluxed CCl_4 via GC retention times and ^{13}C NMR spectra by comparison to a product generated in a blank reaction of silver triflate in CCl_4. Finally, there is apparently a slight dismutation reaction that increases the concentration of dibromoalkane *after* its initial consumption by silver triflate. This was verified by ^1H and ^{13}C NMR in the reactions of 1,3-dibromopropane and 1,4-dibromobutane and by GC analyses of 1,2-dibromoethane product solutions; however, it was not seen in the latter case by either ^1H or ^{13}C NMR analysis. Similar disproportionation in the solvolysis of 3-bromobutyl triflate[15] was postulated to arise from this triflate ester reacting with "free" bromide ions generated by its own decomposition.

Several attempts were made to employ acetonitrile solvent, which has a reflux temperature nearly the same as benzene and CCl_4. This proved totally unsatisfactory when the silver triflate attacked the acetonitrile itself in a reaction highly competitive with that of the bromoalkanes.

Reaction Temperature/Time. Reaction temperature and time significantly influence triflate product yields and stability. Either parameter, if too severe, promotes triflate products' thermal degradation and results in a subsequent alkylation reaction in benzene solvent or a cationically initiated alkene polymerization in CCl_4. Reaction of 1,5-dibromopentane with silver triflate in benzene produces a dark solution with white triflic acid fumes after 20 h of reflux. This problem is circumvented by reducing the reaction temperature, but only with a sacrifice in the amount of ditriflate product (Table I). While a 100% ditriflate conversion would be expected from a 20-h reflux with 1,5-dibromopentane, based upon the 1,4-dibromobutane result, the lower temperature must be used to avoid unacceptable product decomposition, and a 65% conversion to ditriflate results. 1,6-Dibromohexane behaved similarly to 1,5-dibromopentane at the 80 and 54 °C reaction temperatures over 20 h, and subsequent investigation revealed that the initial triflate products were alkylating the benzene solvent. A mechanistic study of alkyl monotriflate alkylations of benzene derivatives has been reported,[24] wherein triflic acid acted as a catalyst. In our reactions, the monobromohexyl triflate and hexanediyl ditriflate products produced over five benzene alkylation products, including **5**–**9**, in the product ratios shown, plus



20% unidentified products. In all but one case, rearrangement of the alkyl chain resulted prior to aromatic

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electrophilic attack where the triflate group was originally situated. The tetralin derivatives result from intramolecular alkylation of the same benzene molecule at two sites ortho to one another; similar cyclizations of ditriflate products generated in situ in reactions of α,ω-bis(Grignard reagents) with silver triflate have been reported.[25]

We verified the catalytic effect of triflic acid in these solvent alkylations by adding one drop of triflic acid to the triflate products generated from the 1,6-dibromohexane reaction with silver triflate at 55 °C for 20 h. Complete alkylation occurred within ≤5.5 h at reflux. By a different approach, the initial addition of 14 mol % of triflic acid to the 1,6-dibromohexane and silver triflate reactants in benzene at 55 °C provided complete alkylation within ≤30.5 h. The higher α,ω-dibromoalkane alkylation demonstrates the tendency to react as independent monobromoalkanes at each primary bromine site. For example, reaction of 1-bromobutane in benzene with silver triflate at reflux temperature for 3 h produces the corresponding monotriflate in a 77% product conversion. Beyond this time, the methylene triplet of the *n*-butyl triflate's NMR decreases significantly and concurrently produces a new downfield-shifted sextet (δ 2.46), indicating subsequent alkylation to produce rearranged *sec*-butylbenzene.

In contrast to benzene alkylation, the thermal instability of the higher α,ω-dibromoalkane homologues in CCl_4 solvent produces an apparent triflic acid catalyzed cationic polymerization. Intractable tars with concomitant darkening of the reaction solution and emanation of white triflic acid vapors result. Monitoring by ^1H NMR showed the disappearance of initially formed triflate product absorptions with the simultaneous growth of high-field saturated hydrocarbon absorptions. This catalysis of thermal decomposition of triflate products effected by trace amounts of triflic acid must be addressed in handling of the silver triflate reagent. Silver triflate is moderately hygroscopic and is best handled in a glovebag under a dry N_2 atmosphere to prevent the formation of trace amounts of triflic acid. We attempted to deal with this problem in one system by using 2 mol% of sterically hindered Proton Sponge, 1,8-bis(dimethylamino)naphthalene. Concurrent room-temperature reactions of 1,4-dibromobutane with silver triflate in CCl_4 with and without the Proton Sponge produced different rates of 4-bromobutyl triflate formation. After 4.0 h, 41% formed in the Proton Sponge treated reaction, whereas 84% formed in the reaction blank. Still, keeping the silver triflate reagent and glassware dry works best.

A suitable balance between reaction time and temperature is necessary. A 54 °C reaction temperature provides the triflate intermediates from 1,5-dibromopentane and 1,6-dibromohexane reactants, but the 20-h reaction time even at 54 °C was too severe for 1,10-dibromodecane (Table I). A reaction time of 45 min produces 10-bromodecyl triflate in an acceptable amount while the best ditriflate yield required an 11-h reaction. At reflux temperature, a 20-h maximum reaction time in benzene is suitable for 1,4-dibromobutane, however, a 3- to 4-h maximum reaction time is best for the 1-bromobutane analogue. Table III outlines the optimum reaction parameters that have proven best for obtaining 12 different triflate products from their corresponding bromoalkanes. Coupled with the kinetic data in Table II, this information should serve as a reasonable guide in planning the solvent selection, reactant, time, and temperature parameters for other alkyl bromides.

Table III. Optimum Synthesis Conditions for Triflate Esters via Silver Triflate–(Di)Bromoalkane Methathesis

desired product	recommended conditions	expected approx yield, nonisolated, %
n-BuOTf	benzene/reflux/3.5 h	77
$Br(CH_2)_2OTf$	benzene/reflux/7 h	92
$TfO(CH_2)_2OTf$	ref 14	
$Br(CH_2)_3OTf$	benzene/reflux/2 h	66
$TfO(CH_2)_3OTf$	benzene/reflux/20 h	76
$Br(CH_2)_4OTf$	CCl_4/reflux/4 min	100
$TfO(CH_2)_4OTf$	benzene/reflux/7.5 h	63
	benzene/reflux/20 h	73[a]
$Br(CH_2)_5OTf$	benzene/54 °C/1 h	76
$TfO(CH_2)_5OTf$	benzene/54 °C/20 h	65
$Br(CH_2)_6OTf$	benzene/54 °C/1 h	80
$Br(CH_2)_{10}OTf$	benzene/54 °C/45 min	70
$TfO(CH_2)_{6-10}OTf$	benzene/54 °C/11 h	57

[a] Although the reaction with pure reagents proved poorly reproducible (several reactions with different samples of reagents at reflux temperature showed extensive decomposition by 16–20 h), three runs produced $TfO(CH_2)_4OTf$ in isolable quantities with the silver triflate–benzene adduct. One 20.5-h reaction using 1.75 mol equiv (relative to dibromobutane) of AgOTf in this form produced an isolated mixture of $Br(CH_2)_4OTf$ and $TfO(CH_2)_4OTf$ (18:82), the latter yield corresponding to 73% based on silver triflate limiting reagent.

Bromine Atom Position. Bromine atom position in the alkane drastically influences the silver triflate metathesis with both mono- and dibromoalkane reactants, and this influence can potentially promote an asymmetric substitution selectivity not available in the condensation of alcohols with triflic anhydride. The degree of separation between bromine atom terminal substituents greatly affects the degree of mono- and ditriflate substitution as well as product stability. In primary dibromoalkanes, a separation of five carbons or more enables the two terminal bromine substituents to behave independently as if they were separate monobromoalkane reactants. Therefore, [illegible] With 1,4-dibromobutane, ^1H and ^{19}F NMR spectra of reaction aliquots revealed an orderly, stepwise metathesis that would permit selective bromine displacement at each bromine site to obtain an asymmetrically disubstituted derivative.

With monobromoalkanes, the secondary bromine atoms in 2-bromopropane and 2-bromobutane are readily displaced at room temperature in CCl_4 solvent; however, substitution of primary bromine atoms in 1-bromobutane requires an elevated temperature in benzene. This reactivity difference between primary and secondary bromine atoms and its potential for selective asymmetric substitution were demonstrated with 1,2-dibromopropane and silver triflate. The 1-bromo-2-propyl triflate ester readily formed at room temperature in CCl_4 and predominated significantly over the 2-bromo-1-propyl triflate. Secondary ester formation represented 80% of the two isomers with pure silver triflate but increased to 95% with a silver triflate–benzene (2:1) adduct previously characterized and reported.[26] The minor isomer likely comes from a bromide 1,2 shift via a three-membered cyclic bromonium ion and provides direct evidence of halogen 1,2 participation by a dibromoalkane in CCl_4. Displacement of the secondary triflate group with 2-fluoro-2,2-dinitroethanol[27] yielded 2-fluoro-2,2-dinitroethyl 1-bromo-2-propyl ether in good yield. Because of the [illegible]

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dinitroethoxy group, the second metathesis step at the primary bromine did not occur, and even refluxing toluene failed to effect displacement. Alternatively, less electronegative secondary substituents in this primary–secondary vicinal structure, as well as 1,3-, 1,4- and higher homologous dibromoalkanes, *or* vicinal dibromoalkanes with two secondary bromine leaving groups each offer possible stepwise or sequential asymmetric substitution. Further studies are in progress to address this point.

Conclusion

The silver triflate metathesis reaction with bromoalkane compounds for obtaining reactive triflate intermediates is an attractive synthetic complement to the triflic anhydride condensation with alcohols. It offers the possibility of selective, stepwise bromine atom displacement for synthesizing asymmetric, disubstituted derivatives and permits the formation of triflate products with structural moieties such as the oxirane ring system, which are inert toward silver triflate but highly reactive with triflic anhydride.

Isolable primary triflate ester intermediates can be made in excellent yields by silver triflate metatheses with bromoalkane substrates, and highly reactive secondary triflate ester derivatives can be prepared in situ for subsequent one-pot conversion to final products. Because of the very labile nature of the triflate group, which makes it an attractive synthetic intermediate, this metathesis reaction is quite susceptible to at least five reaction parameters with mono- or dibromoalkane reactants: (1) bromine atom separation, (2) bromine atom type, (3) solvent, (4) reaction temperature, and (5) reaction time. How these reaction parameters may determine the reaction mechanism followed is a key to successfully using the silver triflate metathesis approach. Mechanistic studies confirmed an apparent rare example of anchimeric stabilization by a bridging triflate group in the lower α,ω-dibromoalkane homologues. This investigation defines the optimum reaction conditions for a number of mono- and dibromoalkane reactants; but more importantly, it provides a systematic illustration of how reaction parameters must be considered in planning reaction conditions with other bromoalkanes. Further investigations are in progress to define the scope and synthetic utility this metathesis reaction offers.

Experimental Section

Instrumentation. ^{13}C and 90-MHz ^1H NMR spectra were taken on a JEOL FX 90Q FT-NMR spectrometer at 25 °C. GLPC analyses were performed on a Shimadzu GC-9APT with a 7 ft × $\frac{1}{4}$ in. stainless-steel column (10% OV-101 on either 100–120-mesh Chromosorb W-AW or Chromosorb 750) or a Varian Aerograph 2700 chromatograph with a 5 ft × $\frac{1}{4}$ in. column (10% OV-101 on 80–100-mesh Chromosorb W). NMR spectra for the studies of alkylation products from triflates derived from $Br(CH_2)_6Br$ were taken on a Varian T-60 CW NMR (60 MHz for ^1H). Mass spectra were obtained on a Hewlett-Packard 5992 GC–mass spectrometer, infrared spectra were obtained on a Beckman IR-20 spectrophotometer (NaCl plates).

Synthesis. Silver trifluoromethanesulfonate was purchased commercially and recrystallized from benzene. The benzene adduct[28] was desolvated by heating (80–90 °C) overnight in a vacuum oven. Bromoalkanes and dibromoalkanes were distilled before initial use. Solvents were ACS reagent grade. Glassware for reactions was thoroughly washed, air-dried, soaked in [illegible] hydrolysis of the silver triflate, and then vacuum dried.

General Procedure. Silver triflate (1.75 mmol for bromoalkanes or 3.50 mmol for dibromoalkanes) was mixed with [illegible] mL of benzene or CCl_4 at room temperature in a 10- or 15-mL round-bottom flask. Reactions were brought to the desired temperature; silver triflate was dissolved in benzene during the elevated temperature reactions (54 °C or reflux). A Liebig condenser with a Drierite-containing drying tube was used in all elevated temperature reactions and some room-temperature reactions. Reflux reactions were heated by oil baths set to 80–90 °C on calibrated hot plate–stirrers; for some room-temperature reactions, ambient-temperature oil baths were used. The reaction vessel for 54 °C consisted of a custom-blown, jacketed round-bottom flask (~25 mL) with an outer 14/20 joint on both the inner flask and outer (jacket) flask. Refluxing acetone in the outer jacket enveloping the inner reaction flask maintained a constant 54 °C temperature.

Analysis. Reaction aliquots were withdrawn at desired times. Correlations of GLPC and NMR analyses were required to determine compositions of the three possible components: dibromoalkane, bromoalkyl triflate, alkanediyl ditriflate. This correlation was necessary because some alkyl triflates are unstable under GLPC analysis conditions and because of the incomplete resolution of NMR signals from bromoalkyl triflate and the symmetrical dibromide or ditriflate. Calibrations of the GC system were made with known dibromoalkane concentrations. After GLPC analysis, the sample was diluted with deuterated solvent ($CDCl_3$ for CCl_4 or C_6D_6 for benzene) for internal NMR lock. The monotriflate and ditriflate concentrations were then calculated from relative ^1H integrations of the triflate methylene triplet and the bromide methylene triplet. ^1H NMR spectra of solutions in benzene were run with simple homogated decoupling for suppression of the benzene absorption; ^1H NMR data are summarized in Table SI (supplementary material). Conversion of bromoalkenes to triflate products was followed by NMR. The decreasing bromoalkyl methylene triplets absorb in the δ 2.5–3.0 range; the increasing triflate methylene signals come at δ 3.6–3.9. 1-Butyl triflate[28] and the α,ω-alkanediyl ditriflates[7,29] have been described previously; our NMR data are consistent with literature results.

Kinetic Studies. Rate data from reactions of α,ω-dibromoalkanes autocatalyzed by a product (possibly AgBr[19]) correlated well in terms of one of the equimolar coproducts, bromoalkyl triflate:

$$-d[Br(CH_2)_nBr]/dt = k[Br(CH_2)_nBr][Br(CH_2)_nOTf] \quad (4)$$

with an integrated rate expression[18]

$$[Br(CH_2)_nBr]_0^{-1} \ln ([Br(CH_2)_nOTf]/[Br(CH_2)_nBr]) = kt + c \quad (5)$$

Monobromoalkane–silver triflate reactions in benzene at elevated temperature follow the 2.5-order rate expression[20]

$$[RBr]_t^{-1.5} - [RBr]_0^{-1.5} = 1.5k_{2.5}t \quad (6)$$

if $[RBr] = [AgOSO_2CF_3]$. In carbon tetrachloride, $[AgOSO_2CF_3]$ remains constant, so the rate behavior is pseudo first order in [RBr]:

$$\ln ([RBr]_0/[RBr]_t) = k_1t \quad (7)$$

At least three data points were used to determine reaction rate [illegible], with the correlation coefficient > 0.98. Unit concentrations of 1.75 mmol/5 mL of solvent corresponded to a range of 0.325 M (for 1,10-dibromodecane) to 0.339 M (for 1,2-dibromoethane).

Trichloromethyl Triflate. A mixture of 2 mL of CCl_4 (21 mmol) and 0.2 g of $AgOSO_2CF_3$ (0.8 mmol) was refluxed for 18 h in a round-bottom flask fitted with a condenser and Drierite drying tube. The product $CCl_3OSO_2CF_3$ was apparent by NMR and GC but was not isolated. ^{13}C NMR ($CDCl_3$): δ 108.7 (s), 117.8 (q, $J_{C,F}$ = 321.4 Hz, CF_3).

4-Chlorobutyl Triflate. A mixture of 0.398 g (2.32 mmol) of $ClCH_2CH_2CH_2CH_2Br$ (Fairfield Chemical Co.) and 0.500 g (2.50 mmol) of $AgOSO_2CF_3$ in 5.00 mL of CCl_4 was refluxed for 10 min in a round-bottom flask fitted with a condenser and Drierite drying

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tube. The conversion to $Cl(CH_2)_4OTf$ was essentially quantitative by NMR. ^{13}C NMR ($CDCl_3$): δ 26.6 (s, $ClCH_2CH_2$), 28.0 (s, CH_2CH_2OTf), 43.3 (s, $ClCH_2$), 76.0 (s, CH_2OTf), 118.5 (q, J_{CF} = 319.6 Hz, CF_3).

Metathesis of 1,4-Dibromobutane and Silver Triflate in Refluxing CCl_4. Analysis of the products from 1,4-dibromobutane plus silver triflate in refluxing CCl_4 after *7h* showed the following products by ^{13}C NMR ($CDCl_3$), with compositions approximated by signal intensities: 1,4-dibromobutane (5%) [δ 29.6 ($BrCH_2CH_2$), 31.5 (CH_2Br)]; 4-bromobutyl triflate (9%) [δ 27.8 (CH_2CH_2Br), 28.0 (CH_2CH_2OTf), 43.7 (CH_2Br), 75.9 (CH_2OTf)]; 4-chlorobutyl triflate (18%) [δ 26.6 (CH_2CH_2Cl), 28.0 (CH_2CH_2OTf), 43.3 (CH_2Cl), 76.1 (CH_2OTf)]; 1,4-butanediyl ditriflate (68%) [δ 25.3 (CH_2CH_2OTf), 75.3 (CH_2OTf), 118.5 (q, J_{CF} = 319.2 Hz, CF_3)].

2-Fluoro-2,2-dinitroethyl 1-Bromo-2-propyl Ether. In a 50-mL round-bottom flask fitted with a condenser and Drierite drying tube, a mixture of 2.60 g of silver triflate–benzene adduct[26] (8.8 mmol of AgOTf) and 2.02 g of 1,2-dibromopropane (10 mmol) was stirred at room temperature for 18 h.[30] Addition of another 0.8 g of silver triflate–benzene adduct (2.7 mmol of AgOTf) and stirring for another 6.1 h resulted in 83% conversion to 1-bromo-2-propyl triflate by ^1H NMR. After filtration into another 50-mL round-bottom flask, reagents for the displacement of the triflate were added: 1.35 g (8.8 mmol) of 2-fluoro-2,2-dinitroethanol[27] in 10 mL of CCl_4 and 2.0 g (14 mmol) of anhydrous sodium sulfate. After stirring at room temperature for 23 h and flash evaporation of CCl_4, elution of the resulting dark brown oil through 5.0 g of alumina with CCl_4, followed again by flash evaporation of solvent, yielded 1.84 g (67% crude yield) of yellow oil. Chromatography with silica gel/CCl_4 yielded a fraction of dark yellow oil and three fractions of very pale yellow oil, which was ~95% 2-fluoro-2,2-dinitroethyl 1-bromo-2-propyl ether and ~5% 2-fluoro-2,2-dinitroethyl 2-bromo-1-propyl ether by ^1H NMR. The middle pale fraction was analyzed. IR (neat): 2980, 2930 (CH), 1600, 1310 cm^{-1} (NO_2). Anal. Calcd for $C_5H_8BrFN_2O_5$: C, 21.84; H, 2.93; N, 10.19; F, 6.91; Br, 29.05. Found (Galbraith Laboratories): C, 21.71; H, 3.05; N, 10.29; F, 6.97; Br, 28.98. Modified Procedure: 8.407 g of pure (unsolvated) silver triflate (32.7 mmol) and 6.606 g of 1,2-dibromopropane (32.7 mmol) were stirred in 75 mL of CCl_4 at room temperature for 5 h, then 5.041 g of $CF(NO_2)_2CH_2OH$ (32.7 mmol) and 2.261 g of K_2CO_3 (15.4 mmol) were added, and stirring was continued. After 1.1 h, the substitution of triflate appeared to be ~70% complete. After 24 h of stirring at room temperature, the reaction solution was filtered through an alumina pad and washed with 70 mL of CCl_4. Removal of solvent afforded 7.33 g (81% crude yield) of light brown oil. Chromatography on silica gel with CCl_4 yielded 5.75 g of pale yellow oil (64%), identified as a mixture of 80% fluorodinitroethyl 1-bromo-2-propyl ether and 20% fluorodinitroethyl 2-bromo-1-propyl ether. 2-Fluoro-2,2-dinitroethyl 1-bromo-2-propyl ether: ^1H NMR (CCl_4–$CDCl_3$) δ 1.31 (3 H, d, J = 6.2 Hz, CH_3), 3.34 (2 H, d, J = 5.5 Hz, CH_2Br), 3.85 (1 H, m, J = 5.9 Hz, CH), 4.65 [2 H, d, J_{HF} = 17.3 Hz, $CH_2CF(NO_2)_2$]; ^{13}C NMR ($CDCl_3$) δ 18.5 (CH_3), 34.9 (CH_2Br), 67.1 [d, J_{CF} = 19.0 Hz, $CH_2CF(NO_2)_2$], 78.6 (CH), 120.2 [d (b), J_{CF} = 299 Hz, $CF(NO_2)_2$]. 2-Fluoro-2,2-dinitroethyl 2-bromo-1-propyl ether: ^1H NMR (CCl_4–$CDCl_3$) δ 1.65 (d, J = 6.2 Hz, CH_3), 3.64 (m, CH_2Br), 3.82 (d, J = 5.5 Hz, CH_2), 4.65 [d, J_{HF} = 17.3 Hz, $CH_2CF(NO_2)_2$]; ^{13}C NMR ($CDCl_3$) δ 21.9 (CH_3), 44.9 (CH_2Br), 68.6 [d, J_{CF} = 19.0 Hz, $CH_2CF(NO_2)_2$], 78.3 (CH_2), 120.2 [d (b), J_{CF} = 299 Hz, $CF(NO_2)_2$].

Alkylations by Triflate Products from 1,6-Dibromohexane–Silver Triflate. 1,6-Dibromohexane (0.40 g, 1.64 mmol) and 0.901 g of silver triflate–benzene adduct[26] (3.04 mmol of AgOTf) in 5 mL of benzene were refluxed in a foil-wrapped 25-mL round-bottom flask for 20 h. The crude mixture was filtered, and benzene was removed. The residue was redissolved in CCl_4 and run through a Pasteur pipet column of silica gel. Preparative gas chromatography (T_0 = 135 °C for 9 min, ramp at 10 °C/min to 300 °C maximum, He flow 46 mL/min) yielded several fractions. Minor components comprising 20% of total products were not identified; five components previously reported in the literature by other routes were identified: **5** (24%), **6** (25%), **7** (21%), **8** (6%), **9** (4%).

1,2,3,4-Tetrahydro-1,4-dimethylnaphthalene[31] (5): GC, T_r (from air) 6.9 min; ^1H NMR ($CDCl_3$) δ 1.27 (6 H, d, J = 7 Hz, CH_3), 1.7 (4 H, m, CH_2), 2.9 (2 H, m, CH), 7.16 (4 H, s, aromatic); IR (CCl_4) 3070 (m), 3020 (m), 2965 (s), 2935 (s), 2870 (s), 1495 (s), 1470 (s), 1380 (m), 1330 (m), 1060 (m), 700 (m) cm^{-1}; MS, *m/e* (relative intensity) 77 (9), 91 (17), 105 (8), 115 (29), 117 (47), 118 (100), 128 (22), 129 (14), 130 (8), 145 (89) 160 (M^+, 44), 161 (5).

1-Ethyl-1,2,3,4-tetrahydronaphthalene[32] (6): GC, T_r 8.1 min; ^1H NMR ($CDCl_3$) δ 0.95 (3 H, t, J = 7 Hz, CH_3), 1.3–2.0 (6 H, m, CH_3CH_2, 2,3-CH_2), 2.73 (3 H, m, CH and 4-CH_2), 7.04 (4 H, s, aromatic); IR (CCl_4) 3080 (m), 3030 (m), 2980 (s), 2940 (s), 2880 (s), 1500 (s), 1460 (s), 1390 (m), 1360 (w), 1045 (w), 700 (m) cm^{-1}; MS, *m/e* (relative intensity) 77 (2), 91 (17), 115 (13), 116 (7), 128 (8), 129 (9), 131 (100), 132 (9), 160 (M^+, 20), 161 (1).

(5-Bromo-1-methylpentyl)benzene[33] (7): GC, T_r 14.2 min; ^1H NMR ($CDCl_3$) δ 1.31 (3 H, d, J = 7.2 Hz, CH_3), 1.5 (6 H, m, CH_2), 2.7 (1 H, m, CH), 3.35 (2 H, t, J = 6.6 Hz, CH_2Br), 7.25 (5 H, s, aromatic); IR (CCl_4) 3085 (m), 3060 (m), 3015 (s), 2960 (s), 2930 (s), 2860 (s), 1605 (m), 1495 (s), 1455 (s), 1380 (m), 1255 (m), 1235 (m), 1080 (w), 1025 (m), 905 (w), 695 (s), 640 (m) cm^{-1}; MS, *m/e* (relative intensity) 77 (8), 79 (8), 91 (11), 105 (100), 106 (10), 135 (4), 137 (4), 240 (M^+ [^{79}Br], 6), 242 (M^+ [^{81}Br], 7).

(6-Bromohexyl)benzene[34] (8): GC, T_r 15.5 min; ^1H NMR ($CDCl_3$) δ 1.1–1.9 (8 H, m, CH_2), 2.51 (2 H, m, $PhCH_2$), 3.24 (2 H, t, J = 7 Hz, CH_2Br), 6.90 (5 H, s, aromatic); IR (CCl_4) 3100 (m), 3080 (m), 3030 (m), 2997 (m), 2940 (s), 2860 (s), 1615 (m), 1505 (m), 1460 (m), 1265 (s), 1095 (m), 1020 (m), 700 (s) cm^{-1}; MS, *m/e* (relative intensity) 65 (11), 77 (7), 91 (100), 92 (59), 105 (21), 240 (M^+ [^{79}Br], 13), 242 (M^+ [^{81}Br], 14).

1,5-Diphenylhexane[32] (9): GC, T_r = 19.5 min; ^1H NMR ($CDCl_3$) δ 0.8–1.9 (m, CH_2), 1.22 (d, J = 6.7 Hz, CH_3), 2.58 (m, $PhCH_2$), 7.19 (s, aromatic); MS, *m/e* (relative intensity) 77 (10), 79 (10), 91 (35), 105 (100), 106 (12), 133 (8), 145 (2), 238 (M^+, 28), 239 (4).

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Registry No. **5**, 4175-54-6; **6**, 13556-58-6; **7**, 26591-23-3; **8**, 27976-27-8; **9**, 13556-60-0; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_3Br$, 109-64-8; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_5Br$, 111-24-0; $Br(CH_2)_6Br$, 629-03-8; $Br(CH_2)_{10}Br$, 4101-68-2; $Br(CH_2)_3OSO_2CF_3$, 103935-47-3; $Br(CH_2)_3OSO_2CF_3$, 103935-48-4; $Br(CH_2)_4OSO_2CF_3$, 103935-49-5; $Br(CH_2)_5OSO_2CF_3$, 103935-50-8; $Br(CH_2)_6OSO_2CF_3$, 103935-51-9; $Br(CH_2)_{10}OSO_2CF_3$, 103935-52-0; $F_3SO(CH_2)_2OSO_2CF_3$, 18928-34-2; $F_3SO(CH_2)_3OSO_2CF_3$, 18934-33-3; $F_3SO(CH_2)_4OSO_2CF_3$, 18934-34-4; $F_3CSO_2O(CH_2)_5OSO_2CF_3$, 63256-91-7; $F_3CSO_2O(CH_2)_6OSO_2CF_3$, 63256-92-8; $F_3CSO_2O(CH_2)_{10}OSO_2CF_3$, 77312-84-6; CH_3CH_2Br, 106-95-6; C_6H_6, 71-43-2; CCl_4, 56-23-5; $CF_3OSO_2CF_3$, 24401-22-7; $Cl(CH_2)_4Br$, 6940-78-9; silver triflate, 2923-28-6; *sec*-butyl triflate, 60306-26-5; 2-fluoro-2,2-dinitroethanol, 17003-75-7; 2-fluoro-2,2-dinitroethyl 1-bromo-2-propyl ether, 103935-53-1; 2-fluoro-2,2-dinitroethyl 2-bromo-1-propyl ether, 103935-54-2; 4-chlorobutyl triflate, 103935-55-3.

Supplementary Material Available: Table SI, ^1H NMR data on reaction product constituents (2 pages). Ordering information is given on any current masthead page.

(30) This reaction time was not optimized, later study showed that a reaction time perhaps as short as 0.5 h is best. Shackelford, S. A., unpublished results.

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SECTION II.

SELECTIVE SYNTHESES OF MONO- AND BIS(2-FLUORO-2,2-DINITROETHOXY)ALKANES: SCOPE OF THE UTILITY OF TRIFLATE INTERMEDIATES

Trifluoromethanesulfonate esters have come to be recognized as especially useful intermediates for effecting functionalizations of certain organic substrates,[3] even for allowing classical nucleophilic substitutions by notoriously non-nucleophilic species such as polynitroaliphatic alcohols.[4] In a previous report,[5] we showed that α,ω-dibromoalkanes can be readily converted to corresponding ω-bromoalkyl triflates or α,ω-alkanediyl ditriflates with silver triflate salt under appropriate conditions; the metatheses were extensively characterized with respect to reaction conditions and reaction kinetics. Although the second metathesis step to the ditriflate could generally be effected under some conditions for α,ω-dibromoalkanes, stepwise metatheses attempted with 1,2-dibromopropane (with an initial synthesis of 1-bromo-2-propyl triflate and subsequent displacement by 2-fluoro-2,2-dinitroethanol to make 1-bromo-2-(2-fluoro-2,2-dinitroethoxy)propane) proved ineffective because of the inertness of the primary bromide vicinal to the very electrophilic fluorodinitroethoxy substituent. In this paper, we describe solutions to this potential problem of lack of reactivity in routes to incorporation of vicinal electronegative groups by comparing the reactivity of a reactant with two secondary bromines, 2,3-dibromobutane, as well as different primary-secondary dibromoalkanes with greater separations between the leaving groups. This class of primary-secondary dibromides we are designating α,ψ-dibromoalkanes, equivalent to 1,(n-1)-dibromoalkanes.

Additionally, we further demonstrate the utility of triflate esters as intermediates with syntheses of a variety of new monoethers and dietners containing the very electronegative, energetic 2-fluoro-2,2-dinitroethoxy substituent. Although the emphasis of this paper is toward the synthetic utility of this transformation, mechanistic aspects of the reaction systems are described as well.

Results and Discussion

Kinetics. The mechanisms of reactions of α,ψ-dibromoalkanes differ from those reported previously for α,ω-dibromoalkanes in showing a solvent dependence, even for rate laws followed by the reactions. Thus, reactions were autocatalytic in carbon tetrachloride as for α,ω-dibromoalkanes; however, reactions of α,ψ-dibromoalkanes were not autocatalytic in benzene, but rather were pseudo-first-order at room temperature. Pseudo-first-order behavior results from an actual order of 2.5, as previously observed for bromoalkane-silver nitrate reactions,[6] but with silver triflate saturated (therefore at constant concentration) in benzene at room temperature. Kinetic results observed for some of these reactions are summarized in Table I.

Reactions in benzene were initially pseudo-first-order as long as the extent of reaction left silver triflate solid undissolved. Since silver triflate's solubility in benzene at room temperature was determined to be 0.114 M, while bromoalkane reactants were typically 0.34 M initial concentration in the kinetics runs, pseudo-first-order behavior obtained up to an extent of reaction of 66%.

Autocatalysis (possibly by AgBr[7]) of the bromoalkane-silver triflate reactions was previously reported[5] to lead to data correlating with a dependence on concentration of a soluble coproduct, the bromoalkyl triflate:

$$-d[Br(CH_2)_nBr]/dt = k[Br(CH_2)_nBr][Br(CH_2)_nOTf] \quad (1)$$

Although this expression was a valid first approximation, closer inspection of the rate data of other reactions has shown that the integrated rate expression arising from this assumption did not hold closely throughout the entire course of the reaction. When the complex nature of these kinetics was realized, a test using a four-fold excess of silver triflate solid in carbon tetrachloride proved that the system in this solvent involved a genuinely heterogeneous

reaction of bromoalkane solution and silver triflate solid when a first approximation of rate constant by the assumption of eq 1 yielded a value 3.6 $\pm$ 0.6 times that of the system utilizing one equivalent of silver triflate. The complex nature of heterogeneous kinetics[8] involves parameters including the active surface area of solid reactant. The variable nature of this parameter for solid reagents typically used only for synthetic work precludes a precise quantitative analysis of the kinetics for practical purposes. However, for the sake of comparison of the relative rates in different solvents as well as for different reactants, rates which were autocatalytic (i.e., in carbon tetrachloride) are expressed in Table I in terms of the parameter t(50%), the time at which the extent of reaction reached 50%. For comparison, the parameter $t_{1/2}$ (truly applicable only for first-order reactions) is given for the pseudo-first-order reactions in benzene.

We previously reported[5] that the sequent reaction steps for metatheses of 1,3-dibromopropane with silver triflate overlapped significantly, thus allowing formation of only 66% of 3-bromopropyl triflate before the second substitution commenced. This characteristic of relative reaction rates of the two steps of the general reaction

$$\underset{R = H,\ CH_3}{Br(CH_2)_nCRHBr} \xrightarrow[k_1]{AgOTf} Br(CH_2)_nCRHOTf \xrightarrow[k_2]{AgOTf} TfO(CH_2)_nCRHOTf \qquad (2)$$

seems general for reactions of dibromoalkanes with a separation of two methylene groups between bromine leaving groups (e.g., 1,3-dibromopropane or 1,3-dibromobutane). In the case of 1,3-dibromobutane, the effect is so pronounced in benzene (a solvent in which silver triflate is well solvated) that $k_2 > k_1$, and only 1,3-butanediyl ditriflate is formed as a product in this system. In contrast, the substitutions still occur stepwise in the heterogeneous reaction in carbon tetrachloride and in chloroform. (A brief study of other solvents showed that nitromethane also produced 1,3-butanediyl ditriflate as a sole

product. Although the rate was not measured quantitatively, it was qualitatively observed to be between that in benzene and in carbon tetrachloride.)

Mechanisms. The differences in observed rate laws are related to differences in mechanism followed by the dibromoalkane reactions. The differences are also manifested as drastically different rates of reaction depending on solvent. Thus, we propose that the autocatalytic S_N1Ag^+ reactions[7] in CCl_4 proceed in the first step via anchimeric assistance by the bridging primary bromide of displacement of the secondary bromide. These reactions proceed approximately 14 times faster in CCl_4 at 0 °C than in benzene at room temperature, with equivalent dibromoalkane concentrations. (The room temperature reaction of 1,2 dibromopropane is 44 times faster in CCl_4 than in benzene.)

The occurrence of the phenomenon of anchimeric assistance[9,10] in the reactions of α,ψ-dibromoalkanes is suggested by the absence of an observable hydride shift (i.e., rearrangements to more stable secondary or tertiary isomers) as well as by the significant rate enhancement in CCl_4 relative to benzene solvent. By reasoning expounded previously for the ω-bromo-α-alkyl triflate system,[5] it is also apparent that anchimeric stabilization by the triflate substituent occurs in the second displacement step of these metathesis starting with 1,3-dibromobutane when $k_2 > k_1$, as observed in benzene, so that the triflate-assisted displacement of the remaining primary bromide is at least slightly faster than the non-assisted initial displacement of secondary bromide. In general, it seems that the behavior of 1,3-dibromoalkanes is characteristic in showing nearly equal rates of the first and second substitutions by silver triflate; this has been true of 1,3-dibromopropane and 1,3-dibromobutane. The phenomena of anchimeric assistance are depicted in the Scheme.

It is of interest that Peterson and coworkers did not observe 1,3-halogen participation in solvolyses of 3-halo-1-butyl nitrobenzenesulfonates,[11] whereas

the analogous triflates did exhibit 1,3-halogen participation.[12] With ω-halo-2-alkyl esters, anchimeric assistance was postulated from rate data, but was not observed via halogen-shifted products.[11,13] In our systems, 1,2-halogen participation was clearly demonstrated by the isolation of halogen-shifted isomers of 2-fluoro-2,2-dinitroethyl ethers formed via the triflates;[5] and 1,3-halogen participation is clearly evidenced by the rate enhancements shown in Table I, though a halogen shift did not occur, similarly to the previous ω-halo-2-alkyl sulfonates.[13]

In addition to the significantly lower reaction rates, the absence of anchimeric assistance in benzene is suggested by the trend in rate data for the homologous series of α,ψ-dibromoalkanes. As expected, the electronegative inductive effect of neighboring bromides is manifested as monotonically increasing rates with increasing separation, approaching that of a reactant with no α-bromo substituent, 2-bromobutane. The inductive effect is most dramatically evidenced in the differences between 1,3- and 1,4-dibromide separations, both in carbon tetrachloride and benzene. In benzene, the ratio of reaction half-times is 33; in CCl_4, it is greater than 29, with accurate measurement precluded by the fast reaction of 1,4-dibromopentane.

Synthetic Utility (Ethers of 2-Fluoro-2,2-dinitroethanol). This model alcohol[4,14] is employed as an example of a very weak nucleophile to demonstrate the useful (and potentially unique) approach offered by the route with triflate esters as intermediates. The particular route demonstrated with bromoalkane and silver triflate reactants is also unique in offering generally excellent selectivity and mild reaction conditions. In particular, bromoalkane precursors can be used when analogous alcohols are unavailable. Second, certain structural moieties are susceptible to attack by triflic anhydride, which would be used in the alternative alcohol-anhydride route. For example, oxacycloalkane rings (such as epoxides) are generally cleaved by triflic anhydride,[15] whereas epi-

bromohydrin reacts with silver triflate to produce the desired 2,3-epoxypropyl triflate.[16] Finally, the stepwise, selective formations of monobromoalkyl triflates, monoethers derived from them, and ultimate diethers from subsequent displacements are demonstrated here by the syntheses of new ethers of fluorodinitroethanol as summarized in Table II.

Particularly noteworthy are the syntheses of the first diethers with vicinal fluorodinitroethoxy substituents; the vicinal incorporation of such electronegative alkoxy substituents is difficult or impossible by other conventional methods. 1,2-Bis(2-fluoro-2,2-dinitroethoxy)propane was synthesized once with an overall conversion of 10% based on 1,2-dibromopropane utilizing the minor isomer of fluorodinitroethyl 2-bromo-1-propyl ether fortuitously formed via a 1,2-halogen shift in 1-bromo-2-propyl triflate, as reported previously.[5] An alternative route to vicinally substituted fluorodinitroethyl alkyl ethers was to modify the substrate so that both leaving groups would be secondary; as an example, 2,3-dibromobutane was used as a model reactant. In this case, the first metathesis and subsequent nucleophilic substitution occur facilely at room temperature. Subsequent reaction of 2-bromo-3-(2-fluoro-2,2-dinitroethoxy)butane occurs with silver triflate, then fluorodinitroethanol, in CCl_4 at 50 °C, with a total conversion to 2,3-bis(2-fluoro-2,2-dinitroethoxy)butane of 15% based on 2,3-dibromobutane. In most cases, reaction conditions were <u>not</u> explored extensively to optimize yields.

As further extensions of the applicability of this transformation to the synthesis of electronegatively substituted ethers, preliminary attempts were made to characterize the behavior of certain other structural types of reactants. The reactivity of tertiary bromides in pinacol dibromide (2,3-dibromo-2,3-dimethylbutane) was sufficiently great that triflate intermediates spontaneously decomposed (presumably via triflic acid elimination) even at low tem-

peratures in inert solvents.

Conclusion

The selectivity of the substitution of readily available bromoalkane reactants by even very non-nucleophilic alcohols via triflate intermediates has been proven by the stepwise syntheses of a variety of mono- and disubstituted alkyl substrates with fluorodinitroethoxy substituents.

The reactivity of α,ψ-dibromoalkanes offers an advantage over that of α,ω-dibromoalkanes in that successive steps are generally more distinct, except that 1,3-dibromoalkanes exhibit unusual behavior in showing nearly equal rates of the successive displacement reactions. 1,3-Dibromopropane could be converted to 3-bromo-1-propyl triflate to the extent of only 66% before 1,3-propanediyl ditriflate formed. Although the reaction of 1,3-dibromobutane could be conducted stepwise in carbon tetrachloride, the second step was faster in benzene or in nitromethane, so that the sole product was 1,3-butanediyl ditriflate.

The generality of the transformation of bromoalkanes to alkyl triflates, and subsequent conversion to alkyl ethers, is a natural conclusion since its success using the very non-nucleophilic fluorodinitroethanol is now demonstrated. More nucleophilic alcohols, especially those sufficiently economical to use as solvents, would greatly facilitate the reactions involved in this synthetic route.

Experimental Section

Materials. Silver trifluoromethanesulfonate was purchased from PCR/SCM Specialty Chemicals and recrystallized from benzene. The silver triflate-benzene adduct[17] was desolvated by heating (80-90 °C) overnight in a vacuum oven. Bromoalkanes were purchased commercially and distilled before initial use. Solvents were ACS reagent grade. 2-Fluoro-2,2-dinitroethanol[14] is not a commercial product, but samples were obtained from the Rocketdyne Division of Rockwell International (Canoga Park, CA) and Fluorochem, Inc. (Azusa, CA).

Reaction Kinetics. Glassware for all reactions was thoroughly washed, air-dried, soaked in 2-propylamine to alleviate potential problems of acidic residue from hydrolysis of the silver triflate, and then vacuum-dried. For kinetic analyses by NMR spectrometry, solvents used were carbon tetrachloride or benzene-d_6. In a typical reaction, 1.75 mmol silver triflate was mixed with 5.00 mL solvent in a 10-mL round-bottom flask; the mixture was brought to the desired reaction temperature; 1.75 mmol (di)bromoalkane was added; reaction aliquots were withdrawn at desired times for analysis. CCl_4 reactions were diluted with $CDCl_3$ for internal NMR lock. Conversion of bromoalkanes to triflate products was followed by ^1H NMR (90 MHz) with a JEOL FX-90Q FT-NMR spectrometer. NMR analyses of reactions run at 0 °C were also carried out at 0 °C.

α,ψ-Dibromoalkane-silver triflate reactions in benzene follow the 2.5-order rate law[6]

$$-d[RBr]/dt = k_{2.5}[RBr][AgOTf]^{1.5} \quad (3)$$

At room temperature, silver triflate is saturated, so the rate behavior is pseudo first order in [RBr]:

$$\ln([RBr]_0/[RBr]_t) = k_1 t \quad (4)$$

Values of t(50%) for reactions in CCl_4, as shown in Table I, were determined by graphical interpolation to 50% completion.

1,2-Bis(2-fluoro-2,2-dinitroethoxy)propane (3). An 80:20 mixture of **1** and **2** was synthesized as reported previously,[5] and the yield of purified monoethers was improved to 78%. Unfortunately, most attempts to perform further substitution on this intermediate were unsuccessful. In one experiment which produced **3**, 0.481 g (1.75 mmol) of the mixture of **1** and **2** in 2 mL CCl_4 was added to a slurry of 0.450 g AgOTf (1.75 mmol) in 3 mL CCl_4. The solution was refluxed for 2.25 h, then cooled to room temperature. Fluorodinitroethanol (0.270 g, 1.75 mmol) was added; after 3 h, 0.121 g K_2CO_3 (0.875 mmol) was added. The solution

was left overnight then filtered through a pad of alumina. Concentration of this solution yielded a mixture containing 3 as a component, evidenced by ^{13}C NMR, to the extent of 13% in the presence of unreacted 1 and 2. 3: ^{1}H NMR ($CDCl_3$) δ 1.28 (d, CH_3), 3.48 (d, CH_2), 3.83 (m, CH), 4.68 (d, CH_2CF); ^{13}C NMR ($CDCl_3$) δ 17.8 (CH_3, 47.1 (CH_2), 67.4 (d, $\underline{C}H_2CF$), 79.1 (CH), 120.2 (d, $CF(NO_2)_2$).

1-Bromo-3-(2-fluoro-2,2-dinitroethoxy)butane (4). Silver triflate (1.285 g, 5.00 mmol) was stirred in 15 mL CCl_4 in a stoppered 25-mL flask and cooled to 0 °C. 1,3-Dibromobutane (1.080 g, 5.00 mmol) was added to this slurry, stirring. After 80 min, 0.770 g fluorodinitroethanol (5.00 mmol) and 0.346 g K_2CO_3 (2.50 mmol) were added, and the stopper was replaced with a Drierite drying tube. The ice bath was removed after 100 min more. The solution was stirred overnight at ambient temperature, then was filtered through a pad of alumina. Chromatography on silica gel-CCl_4 yielded a golden-colored oil, 4 (0.960 g, 66%), which was distilled at 58-60 °C (50 μm). 4-Bromo-2-butyl triflate: ^{1}H NMR ($CDCl_3$) δ 1.61 (d, CH_3), 2.24 (m, $C\underline{H}_2CH$), 3.45 (m, CH_2Br), 5.24 (m, CH); ^{13}C NMR ($CDCl_3$) δ 21.0 (CH_3), 26.8 ($\underline{C}H_2CH$), 38.9 (CH_2Br), 86.2 (CH), 118.0 (q, CF_3). 4: ^{1}H NMR ($CDCl_3$) δ 1.23 (d, CH_3), 2.01 (m, $C\underline{H}_2CH$), 3.41 (m, CH_2Br), 3.91 (m, CH), 4.60 (dd, J_{HF} = 17.3 Hz, $C\underline{H}_2CF$); ^{13}C NMR ($CDCl_3$) δ 18.4 (CH_3), 28.9 ($\underline{C}H_2CH$), 39.1 (CH_2Br), 66.2 (d, $^{2}J_{CF}$ = 19 Hz, $O\underline{C}H_2CF$), 76.6 (CH), 120.5 (d, $^{1}J_{CF}$ = 294 Hz, $CF(NO_2)_2$).

1,3-Bis(2-fluoro-2,2-dinitroethoxy)butane (5). Silver triflate (0.514 g, 2.0 mmol) was dissolved in 5 mL nitromethane in a 10-mL flask, and the solution was cooled to 0 °C in an ice bath. To this was added 0.432 g 1,3-dibromobutane (2.0 mmol) in 1 mL nitromethane. After 40 min, the ice bath was removed; after 1 h total, 0.308 g fluorodinitroethanol (2.0 mmol) was added, followed in 3 min by 0.138 g K_2CO_3 (1.0 mmol). Chromatography on alumina with CCl_4 followed by CH_2Cl_2 yielded 0.344 g (48%) of light yellow oil, 5. 1,3-Butanediyl ditriflate:

^{1}H NMR (CD_3NO_2) δ 1.62 (d, CH_3), 2.41 (m, $C\underline{H}_2CH$), 3.59 (CH_2OTf), 5.41 (CHOTf); ^{13}C NMR (CD_3NO_2) δ 28.9 (CH_3), 33.2 ($\underline{C}H_2CH$), 51.1 (CH_2OTf), 90.4 (CHOTf). **5**: ^{1}H NMR ($CDCl_3$) δ 1.25 (d, CH_3), 2.02 (m, $C\underline{H}_2CH$), 3.49 (CH_2OTf), 4.0 (CHOTf); ^{13}C NMR (CD_3NO_2) δ 22.4 (CH_3), 29.8 ($\underline{C}H_2CH$), 40.8 (CH_2OTf), 67.3 (CHOTf).

2-Bromo-3-(2-fluoro-2,2-dinitroethoxy)butane (6). 2,3-Dibromobutane was a mixture of 20% dl and 80% meso isomers manufactured by Tokyo Kasei. Silver triflate (0.450 g, 1.75 mmol) with 3 mL CCl_4 in a 10-mL flask was cooled in an ice-water bath. 2,3-Dibromobutane (0.378 g, 1.75 mmol) in 2 mL CCl_4 was added. After stirring at 0 °C for 17 min, 0.121 g K_2CO_3 (0.875 mmol) and 0.270 g fluorodinitroethanol (1.75 mmol) were added. The mixture warmed to ambient temperature over the next 3.5 h, then it was filtered through pad of alumina. Chromatography on silica gel-CCl_4 yielded 0.382 g (76%) of light yellow liquid, which darkened on standing over a week. This was distilled at 54-58 °C (2-3 μm), yielding a clear liquid. 3-Bromo-2-butyl triflate: ^{1}H NMR ($CDCl_3$) δ 1.64 (d, $C\underline{H}_3CHOTf$), 1.74 (d, $C\underline{H}_3CHBr$), 4.18 (m, CHBr), 4.98 (m, CHOTf). **6**: ^{1}H NMR ($CDCl_3$) δ 1.28 (d, $C\underline{H}_3CH$-O-), 1.62 (d, $C\underline{H}_3CHBr$), 3.73 (m, CH-O-), 3.99 (m, CHBr), 4.67 (d, OCH_2CF). The enantiomeric pairs formed from dl- and meso-2,3-dibromobutane could be distinguished by ^{13}C NMR and were formed in a ratio essentially unchanged from the starting material. (2R,3R)- and (2S,3S)-2-Bromo-3-(2-fluoro-2,2-dinitroethoxy)butane: ^{13}C NMR ($CDCl_3$) δ 16.0 ($\underline{C}H_3CHBr$), 21.0 ($\underline{C}H_3CH$-O-), 50.3 (CHBr), 67.3 (d, OCH_2), 82.6 (CH-O-), 120.6 (d, $CF(NO_2)_2$). (2R,3S)- and (2S,3R)-2-Bromo-3-(2-fluoro-2,2-dinitroethoxy)butane: ^{13}C NMR ($CDCl_3$) δ 17.0 ($\underline{C}H_3CHBr$), 20.6 ($\underline{C}H_3CH$-O-), 51.0 (CHBr), 67.5 (d, OCH_2), 82.6 (CH-O-), 120.6 (d, $CF(NO_2)_2$).

2,3-Bis(2-fluoro-2,2-dinitroethoxy)butane (7). **6** (0.434 g, 1.5 mmol) in 4 mL CCl_4 was added to 0.385 g (1.5 mmol) AgOTf in a 10-mL flask. The mixture was warmed to 57 °C in an oil bath. After 47 min, 0.234 g (1.5 mmol) fluorodinitro-

ethanol in 2 mL CCl_4 was added. After another 45 min, 0.138 g (1.0 mmol) K_2CO_3 was added; after another 45 min, the oil bath heat was turned off and the solution stirred overnight at ambient temperature. The solution was then filtered through a pad of alumina. Chromatography on silica gel-CCl_4 yielded 0.256 g of light yellow oil, which was a mixture of starting material and product. Medium-pressure liquid chromatography (Ace Glass Michel-Miller system) on silica gel-hexane/chloroform yielded 0.120 g (22%) of **7**, which appeared to be exclusively the meso enantiomeric pair, perhaps for reasons of steric hindrance in nucleophilic substitution by fluorodinitroethanol. meso-2,3-Bis(2-fluoro-2,2-dinitroethoxy)butane: ^{1}H NMR ($CDCl_3$) δ 0.90 (d, CH_3), 1.93 (m, CH), 4.58 (d, OCH_2); ^{13}C NMR ($CDCl_3$) δ 17.2 (CH_3), 63.1 (OCH_2), 109.2 (CH), 120.6 ($CF(NO_2)_2$).

1-Bromo-4-(2-fluoro-2,2-dinitroethoxy)pentane (8). 1,4-Dibromopentane (8.04 g, 35 mmol) was added to a slurry of 9.00 g AgOTf (35 mmol) in 50 mL $CHCl_3$ at 0 °C in a 100-mL flask with stirring. After 1 min, 5.40 g fluorodinitroethanol (35 mmol) was added. After 5 min more, 4.97 g Na_2SO_4 (35 mmol) was added. The mixture was left at 0 °C for 6.5 h, then was left at ambient temperature overnight. The solution was filtered through a pad of alumina along with 100 mL $CHCl_3$. This solution was washed twice with 100-mL portions of dilute aqueous sodium bisulfite, then twice with 100-mL portions of water; the chloroform layer was dried over sodium sulfate. Chromatography on silica gel-CCl_4 yielded 6.824 g (64%) of light yellow oil, which was distilled at 74-76 °C (3-4 μm). 5-Bromo-2-pentyl triflate: ^{1}H NMR ($CDCl_3$) 1.58 (d, CH_3), 1.96 (m, CH_2), 3.46 (t, CH_2Br), 5.09 (m, CH). **8**: ^{1}H NMR ($CDCl_3$) δ 1.20 (d, CH_3), 1.73 (m, CH_2), 3.41 (t, CH_2Br), 3.69 (m, CH), 4.56 (d, OCH_2CF); ^{13}C NMR ($CDCl_3$) δ 18.5 (CH_3), 28.0 ($\underline{C}H_2CH$), 33.3 ($\underline{C}H_2CH_2Br$), 34.3 (CH_2Br), 65.8 (d, OCH_2), 78.1 (CH), 120.6 (d, $(NO_2)_2$).

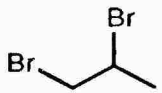
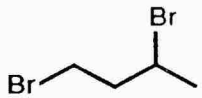
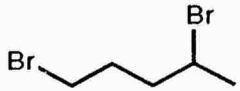
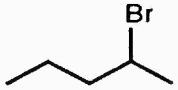
1,4-Bis(2-fluoro-2,2-dinitroethoxy)pentane (9). 8 (0.758 g, 2.5 mmol) was

added to a slurry of 0.642 g AgOTf (2.5 mmol) in 5 mL CCl_4 at room temperature with stirring in a 10-mL flask. After 30 min, 0.385 g fluorodinitroethanol (2.5 mmol) and 0.173 g K_2CO_3 (1.25 mmol) were added. The flask was fitted with a Drierite drying tube and left overnight. The solution was then filtered through a pad of alumina. Chromatography on silica gel-CCl_4 yielded 0.434 g (46%) of a yellow oil which was an 84:16 mixture of **9** with another isomer of bis(2-fluoro-2,2-dinitroethoxy)pentane, according to the ^{13}C NMR spectrum. Separation by medium-pressure liquid chromatography (Ace Glass Michel-Miller system) on silica gel-hexane/chloroform yielded pure **9** in overall 39% yield from **8**.

Reaction Attempts with Pinacol Dibromide. 2,3-Dibromo-2,3-dimethylbutane (Tokyo Kasei) was recrystallized from ethanol to white needles. Reactions of this material with one equivalent of silver triflate were attempted under a variety of reaction conditions: benzene at room temperature, carbon tetrachloride at -20 °C, nitromethane at -20 °C; additionally, under conditions of NMR analysis to obtain spectra immediately, in CD_2Cl_2 at -50 °C as well as in $CDCl_3$ at -20 °C. In all cases, reaction appeared to occur by visual evidence (e.g., formation of AgBr solid in initially homogeneous nitromethane solution), but in all cases the only products apparent by NMR analysis of solution phases were starting material and small amounts of presumed polymer(s) with NMR absorptions upfield of the pinacol dibromide methyl peaks.

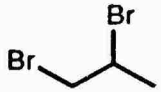
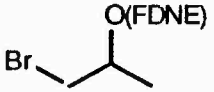
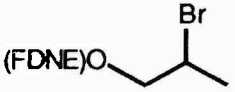
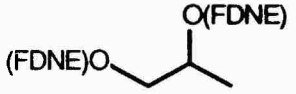
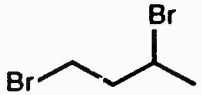
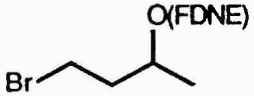
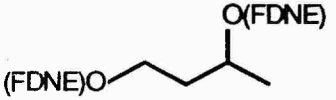
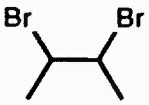
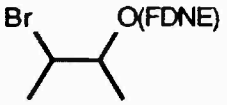
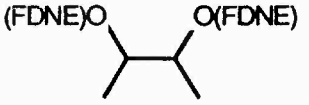
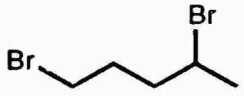
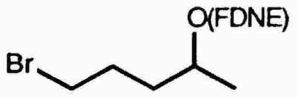
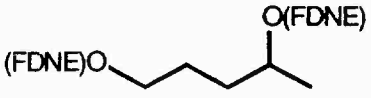
Acknowledgment. Financial support of the Air Force Office of Scientific Research/Directorate of Chemical and Atmospheric Sciences is gratefully acknowledged.

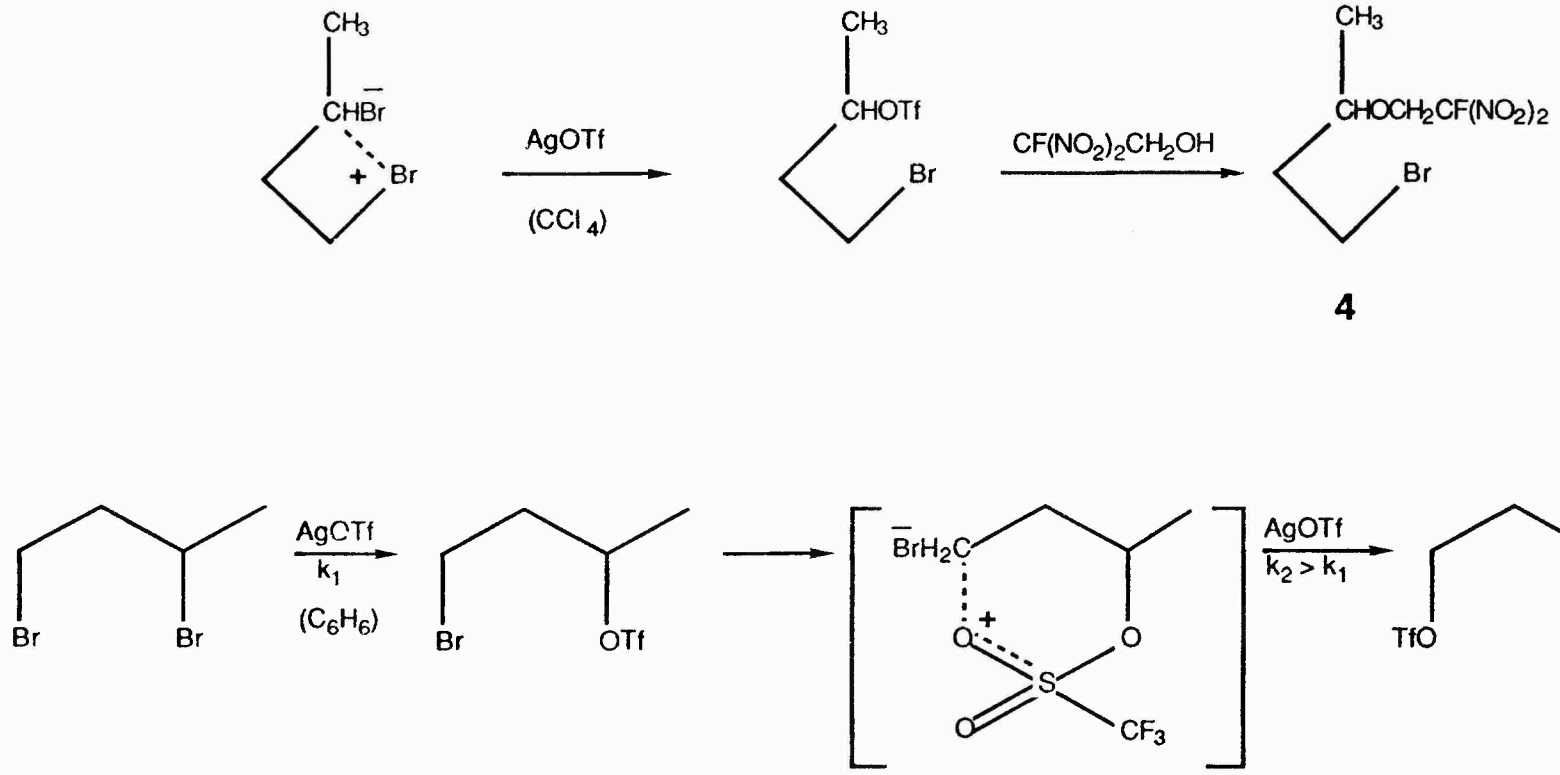
Table I. Kinetic Parameters of Silver Triflate-(Di)bromoalkane Reactions[a]

Solvent	temp	Reactant:				
C_6D_6	room temp	10^5k_1, s^{-1}	1.0	1.5	49	91
		$t_{1/2}$, h	19	13	0.40	0.21
CCl_4	room temp	t(50%), h	0.42			
	0 °C	t(50%), h	1.41	0.86	<0.03	

[a] Reaction scale: 1.75 mmol of (di)bromoalkane + 1.75 mmol AgOTf in 5 mL of solvent.

Table II. New Fluorodinitroethyl Ether Derivatives

Reactant	Fluorodinitroethyl (FDNE) ether products
	 **1**  **2**
	 **3**
	 **4**
	 **5**
	 **6**
	 **7**
	 **8**
	 **9**



Scheme. Anchimeric assistance by bromide and triflate

References and Notes

(1) Presented in part at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, September 1986 (ORGN 21).

(2) Research conducted at AFRPL (1980-1984).

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