increasing solvent polarity at low temperature and have suggested an explanation based on a solvent compression effect[51] to explain this anomaly. According to this proposal,[51] the population of the conformer with the smaller molar volume (the axial conformer) should increase with the more polar solvent owing to higher internal pressure exerted by the solvent. An alternate explanation advanced by Fuchs et al.[52] suggests that when the molecular dipoles of the axial and equatorial conformers are of similar magnitudes, the more polar double-bond no-bond structure,[53] resulting from hyperconjugative interactions in the axial conformer, will be stabilized in the more polar solvent.

Regardless of the exact explanation for the anomalous solvent dependence of the equilibria of 1–8, it is clear from the data in Table IV that similar substituent effects are observed in nonpolar and polar solvents. If dipolar interactions were important, then a marked substituent effect on ΔG° would not be observed in a polar solvent. The data suggest, therefore, that dipole/dipole interactions do not have a dominating influence. In fact, the appearance of a large proportion of the axial conformers even in a polar medium suggests that other electronic factors are important. It is noteworthy that Cantacuzene and Tordeux[34] have observed no substituent effect on the conformational equilibria of 2-(4-substituted-phenoxy)cyclohexanones in the polar solvent CD_3CN and Ouedraogo and Lessard[32] have noted a lesser sensitivity of the conformational equilibria in 2-(4-substituted-phenoxy)tetrahydropyrans to the effect of the substituent in a polar medium.

The solvent and *temperature* dependence of the equilibria in 2-(arylseleno)-1,3-dithianes is being studied in greater detail in order to evaluate the enthalpic and entropic contributions to the conformational free energies, and the results will be reported in a separate study.

Conclusions

Conformational analysis of 2-[(4-substituted-phenyl)seleno]-1,3-dithianes in solution by means of ^{1}H and ^{77}Se NMR spectroscopy indicates that the magnitude of the anomeric effect varies with substituent in the order $NO_2 > CF_3 > Cl > F \approx H > Me > OMe > NMe_2$, providing systematic evidence for the role of stabilizing orbital interactions operating in S–C–Se fragments. The postulate is reinforced by analysis of the data by means of a dual substituent parameter approach which suggests that increased electron density is present on selenium in the axial conformers. The latter conclusion is also substantiated by trends in ^{13}C NMR and ^{77}Se NMR shifts for the axial and equatorial conformers. The solvent dependence of the conformational equilibria for selected compounds shows no apparent correlation with dielectric constant although significant anomeric effects and substituent effects are still observed in a polar medium. The results are interpreted in terms of the dominance of the orbital interaction component over the electrostatic component.

Acknowledgment. We are grateful to Lise Bramall for the statistical analysis of results, Professors M. J. Gresser and E. Juaristi for helpful discussions, and the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Tables S-I, S-II, S-III, S-IV, and S-V (8 pages). Ordering information is given on any current masthead page.

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Selective Syntheses of Mono- and Bis(2-fluoro-2,2-dinitroethoxy)alkanes: Scope of the Utility of Triflate Intermediates[1]

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While displacement of bromide in 1-bromo-2-(2-fluoro-2,2-dinitroethoxy)propane (1) cannot be effected by silver trifluoromethanesulfonate because of the electronegative vicinal alkoxide's deactivating inductive effect on the primary bromine, substituents in the secondary position are more labile with respect to nucleophilic displacement. The scope of the utility for conducting nucleophilic substituents using homologous α,ψ-dibromoalkanes [1,(n − 1)-dibromoalkanes] and a vicinal dibromoalkane, 2,3-dibromoalkane, is reported. This approach produced a variety of new fluorodinitroethyl ethers (3–9), including the novel 2,3-bis(2-fluoro-2,2-dinitroethoxy)butane (3)—which possesses two electronegative alkoxy substituents in a vicinal arrangement—from the fortuitous intermediate 2-bromo-1-(2-fluoro-2,2-dinitroethoxy)propane (2) by way of anchimeric assistance in the reaction of 1,2-dibromopropane, also yielding 1, the regioisomer of 2. Typically, α,ψ- and α,ω-dibromoalkanes are distinctly stepwise in their two possible S_N1Ag^+ displacements of bromide by silver triflate, a characteristic which allows selective incorporation of relatively nonnucleophilic alkoxy substituents via displacements 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 nonnucleophilic 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 me-

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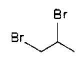
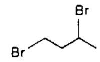
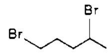
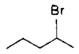
Table I. Kinetic Parameters of Silver Triflate-(Di)bromoalkane Reactions[a]

			reactant			
solvent	temp					
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 of AgOTf in 5 mL of solvent.

tatheses 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, via 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 (**1**), proved ineffective because of the inertness of the primary bromide vicinal to the very electrophilic fluorodinitroethoxy substituent. In this paper, two approaches are reported that provide a solution to this reactivity problem. The greater reactivity of secondary bromide substituents with respect to nucleophilic displacement with silver triflate was exploited by using 2,3-dibromobutane, in which (unlike 1,2-dibromopropane) both vicinal bromine substituents are in the secondary position. While the second secondary bromine was deactivated toward nucleophilic displacement by the initial substitution of a vicinal fluorodinitroethoxy group, its reactivity remained high enough to permit further stepwise reaction with the silver triflate reagent. Second, different primary–secondary dibromoalkanes with greater separations between the leaving groups were used to attenuate the deactivating influence of the first fluorodinitroethoxy group. This class of primary–secondary dibromides we are designating α,ψ-dibromoalkanes, equivalent to 1,(n − 1)-dibromoalkanes.

The utility of triflate esters as intermediates in the syntheses of various new monoethers and diethers containing the very electronegative, energetic 2-fluoro-2,2-dinitroethoxy substituent is demonstrated here. Although the emphasis of this paper is toward the synthetic utility of this transformation, mechanistic aspects of the reaction systems are also described.

Results and Discussion

Kinetics. The mechanisms of reactions of α,ψ-dibromoalkanes differ from those reported previously[5] for α,ω-dibromoalkanes by 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 the benzene solution is saturated with silver triflate (therefore at a constant salt concentration) 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%.

Possible autocatalysis of the bromoalkane–silver triflate reactions by AgBr[7] in carbon tetrachloride 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 fourfold 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. A first approximation of rate constant by the assumption of eq 1 yielded a value 3.6 ± 0.6 times that of the system utilizing 1 equiv 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 comparing relative reaction rates in different solvents as well as for different reactants, rates which were autocatalytic (i.e., those in carbon tetrachloride) are expressed in Table I in terms of the parameter $t(50\%)$, which represents the time at which the extent of reaction reached 50%. For comparison, the parameter $t_{1/2}$, which is 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 and thus permitted only 66% of complete conversion to 3-bromopropyl triflate before the second substitution commenced. However, this characteristic of relative reaction rates of the two steps of the general reaction

$$Br(CH_2)_nCRHBr \xrightarrow[k_1]{AgOTf} Br(CH_2)_nCRHOTf \xrightarrow[k_2]{AgOTf} TfO(CH_2)_nCRHOTf \quad (2)$$

$$R = H, CH_3$$

seems general for reactions of dibromoalkanes with a separation of three carbons between 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, in which silver triflate is well solvated, that k_2

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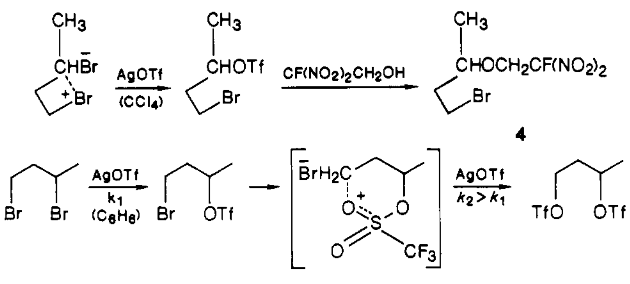
Scheme I



$> k_1$, 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 using carbon tetrachloride or chloroform solvent. 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. These 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 during displacement of the secondary bromide. These reactions proceed approximately 14 times faster in CCl_4 at 0 °C than in benzene at room temperature at 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, by which rearrangements to more stable secondary or tertiary isomers would occur, as well as by the significant rate enhancement found in CCl_4 solvent relative to benzene. 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 benzene solvent during the second displacement step of these metatheses starting with 1,3-dibromobutane when $k_2 > k_1$, wherein the triflate-stabilized displacement of the remaining primary bromide is at least slightly faster than the nonassisted 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 Scheme I.

Interestingly, Peterson and co-workers—who noted general agreement between extent of halogen participation based on analysis of rates and that based on yield of halogen-shifted products—reported relative solvolysis rates of 2-, 3-, 4-, and 5-chloro-1-alkyl nitrobenzenesulfonates in the ratios of 14:1:8100:250 and yields of 1,2-, 1,4-, and 1,5-halogen shifted products of ~1%, 99.5%, and 90%, respectively, suggesting the absence of 1,3-halogen participation.[11] In contrast, 1,3-halogen participation *was* later reported to occur in the triflates when the series of 3-halo-1-butyl sulfonates was extended to other halides, and yields of primary halide products for Cl, Br, and I were 5%, 88%, and 94%, respectively.[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 made evident by the rate enhancements shown in Table I, although a halogen *shift* did not occur, which is behavior similar to that exhibited by 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, which approach that of a reactant with *no* α-bromo substituent, 2-bromobutane. The inductive effect is most dramatically made evident by 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 a more precise 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 synthetic approach offered by using triflate esters as intermediates. Also, the particular synthetic approach demonstrated with bromoalkane and silver triflate reactants often provides excellent product selectivity under mild reaction conditions. In particular, bromoalkane precursors can be used when analogous alcohols are unavailable. Second, certain structural moieties that are highly susceptible to attack by triflic anhydride can be used in this alternative bromoalkane–silver triflate route. For example, oxacycloalkane rings (such as epoxides) are generally cleaved by triflic anhydride;[15] but epibromohydrin reacts with silver triflate to produce the desired 2,3-epoxypropyl triflate.[16] Finally, the stepwise, selective formations of monobromoalkyl triflates, the monoethers derived from them, and the ultimate diethers from subsequent displacements are demonstrated 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 (**3**) was synthesized once with an overall conversion of 10% based on 1,2-dibromopropane using the minor isomer, 2-bromo-1-(2-fluoro-2,2-dinitroethoxy)propane (**2**), fortuitously formed via a 1,2-halogen shift in 1-bromo-2-propyl triflate, as reported previously.[5] Because secondary bromine substituents are more labile with respect to dis-

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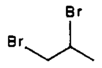
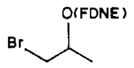
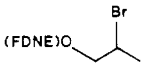
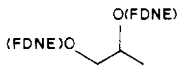
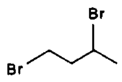
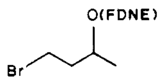
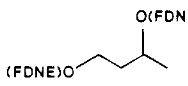
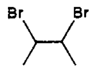
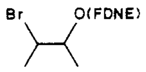
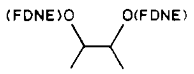
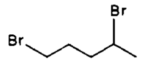
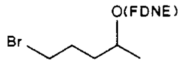
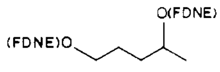
Table II. New Fluorodinitroethyl Ether Derivatives

reactant	fluorodinitroethyl (FDNE) ether products	
	 1[a]  2[a]	 3
	 4	 5
	 6	 7
	 8	 9

[a] Reported previously (ref 5).

placement by silver triflate, an alternative route to vicinally substituted fluorodinitroethyl alkyl ethers came from modifying the substrate so that both leaving groups are in secondary positions, as in the 2,3-dibromobutane model reactant. In this case, the first metathesis and subsequent nucleophilic substitution of the intermediate triflate group occur facilely at room temperature, as with 1,2-dibromopropane. Subsequent reaction of 2-bromo-3-(2-fluoro-2,2-dinitroethoxy)butane occurs at the remaining bromine site with silver triflate and then with fluorodinitroethanol in CCl_4 at 50 °C. A total conversion to 2,3-bis(2-fluoro-2,2-dinitroethoxy)butane of 15% based on 2,3-dibromobutane resulted. Reaction conditions were *not* explored extensively to optimize yields in this case or the others described herein.

Attempts using pinacol dibromide (2,3-dibromo-2,3-dimethylbutane) demonstrated that the tertiary triflate group was sufficiently labile in the corresponding triflate intermediates to induce spontaneous decomposition, presumably via triflic acid elimination, even at low temperatures in inert solvents.

Conclusion

The selective substitution of readily available bromoalkane reactants with very nonnucleophilic alcohols via triflate intermediates has been demonstrated by the stepwise syntheses of various mono- and disubstituted alkyl substrates which contain fluorodinitroethoxy substituents. More nucleophilic alcohols, especially those sufficiently economical to use as solvents, would greatly facilitate the conversions of the alkyl triflate intermediates to ether products.

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). Elemental analyses were determined with a Perkin-Elmer 240C elemental analyzer.

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 of silver triflate were mixed with 5.00 mL of solvent in a 10-mL round-bottom flask; the mixture was brought to the desired reaction temperature; 1.75 mmol of (di)bromoalkane were added; and 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] (eq 3). At room temperature, the solution

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

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

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

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] yielding 78% of purified monoethers (compared to 64% reported previously). Most attempts to perform further substitution on these intermediates were unsuccessful. In one experiment which produced **3**, 0.481 g (1.75 mmol) of the mixture of **1** and **2** in 2 mL of CCl_4 was added to a slurry of 0.450 g of AgOTf (1.75 mmol) in 3 mL of CCl_4. The solution was refluxed for 2.25 h and then cooled to room temperature. Fluorodinitroethanol (0.270 g, 1.75 mmol) was added; after 3 h, 0.121 g of K_2CO_3 (0.875 mmol) was added. The solution was left overnight and then filtered through a pad of alumina. Concentration of this solution yielded a mixture containing **3** as a component, made evident by ^{13}C NMR, to the extent of 13% in the presence of unreacted **1** and **2**. Compound **3**: ^1H 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, CH_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 of 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 of fluorodinitroethanol (5.00 mmol) and 0.346 g of 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 and 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: ^1H NMR ($CDCl_3$) δ 1.61 (d, CH_3), 2.24 (m, CH_2CH), 3.45 (m, CH_2Br), 5.24 (m, CH); ^{13}C NMR ($CDCl_3$) δ 21.0 (CH_3), 26.8

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(CH_2CH), 38.9 (CH_2Br), 86.2 (CH), 118.0 (q, CF_3). Compound 4: ^{1}H NMR ($CDCl_3$) δ 1.23 (d, CH_3), 2.01 (m, CH_2CH), 3.41 (m, CH_2Br), 3.91 (m, CH), 4.60 (dd, J_{HF} = 17.3 Hz, CH_2CF); ^{13}C NMR ($CDCl_3$) δ 18.4 (CH_3), 28.9 (CH_2CH), 39.1 (CH_2Br), 66.2 (d, $^2J_{CF}$ = 19 Hz, OCH_2CF), 76.6 (CH), 120.5 (d, $^1J_{CF}$ = 294 Hz, $CF(NO_2)_2$). Anal. Calcd: C, 24.93; H, 3.49; N, 9.69. Found: C, 25.00; H, 3.52; N, 9.11.

1,3-Bis(2-fluoro-2,2-dinitroethoxy)butane (5). Silver triflate (0.514 g, 2.0 mmol) was dissolved in 5 mL of 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 of 1,3-dibromobutane (2.0 mmol) in 1 mL of nitromethane. After 40 min, the ice bath was removed; after 1 h total, 0.308 g of fluorodinitroethanol (2.0 mmol) was added, followed in 3 min by 0.138 g of 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, CH_2CH), 3.59 (CH_2OTf), 5.41 (CHOTf); ^{13}C NMR (CD_3NO_2) δ 28.9 (CH_3), 33.2 (CH_2CH), 51.1 (CH_2OTf), 90.4 (CHOTf). Compound **5**: ^{1}H NMR ($CDCl_3$) δ 1.25 (d, CH_3), 2.02 (m, CH_2CH), 3.49 ($CH_2CH_2OCH_2$), 4.0 ($CHOCH_2$); ^{13}C NMR ($CDCl_3$) δ 22.4 (CH_3), 29.8 (CH_2CH), 40.8 ($CH_2CH_2OCH_2$), 61.4 (d, CH_2CF), 67.3 ($CHOCH_2$), 120.8 (d, $CF(NO_2)_2$).

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 of 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 of CCl_4 was added. After stirring at 0 °C for 17 min, 0.121 g of K_2CO_3 (0.875 mmol) and 0.270 g of fluorodinitroethanol (1.75 mmol) were added. The mixture warmed to ambient temperature over the next 3.5 h; then it was filtered through a 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, CH_3CHOTf), 1.74 (d, CH_3CHBr), 4.18 (m, CHBr), 4.98 (m, CHOTf). Compound **6**: ^{1}H NMR ($CDCl_3$) δ 1.28 (d, CH_3CHO), 1.62 (d, CH_3CHBr), 3.73 (m, CHO), 3.99 (m, CHBr), 4.67 (d, OCH_2CF). The diastereomers 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. (2*R*,3*R*)- and (2*S*,3*S*)-2-Bromo-3-(2-fluoro-2,2-dinitroethoxy)butane: ^{13}C NMR ($CDCl_3$) δ 16.0 (CH_3CHBr), 21.0 (CH_3CHO), 50.3 (CHBr), 67.3 (d, OCH_2), 82.6 (CHO), 120.6 (d, $CF(NO_2)_2$). (2*R*,3*S*)- and (2*S*,3*R*)-2-Bromo-3-(2-fluoro-2,2-dinitroethoxy)butane: ^{13}C NMR ($CDCl_3$) δ 17.0 (CH_3CHBr), 20.6 (CH_3CHO), 51.0 (CHBr), 67.5 (d, OCH_2), 82.6 (CHO), 120.6 (d, $CF(NO_2)_2$). Anal. Calcd: C, 24.93; H, 3.49; N, 9.69. Found: C, 24.73; H, 3.45; N, 9.35.

2,3-Bis(2-fluoro-2,2-dinitroethoxy)butane (7). Compound **6** (0.434 g, 1.50 mmol) in 4 mL of CCl_4 was added to 0.385 g (1.50 mmol) of AgOTf in a 10-mL flask. The mixture was warmed to 57 °C in an oil bath. After 47 min, 0.234 g (1.50 mmol) of fluorodinitroethanol in 2 mL of CCl_4 was added. After another 45 min, 0.138 g (1.00 mmol) of K_2CO_3 was added; after another 45 min, the oil bath 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 an oil, **7**, which appeared to be exclusively the *meso* enantiomeric pair (an induction based on ^{13}C NMR spectral evidence of a single isomer and the observation that an isolated reaction yield is unlikely to be 100%, as would be required for the assertion of the *dl* isomer as product), perhaps for reasons of steric hindrance in nucleophilic substitution by fluorodinitroethanol. The oil solidified to a white solid upon standing several months refrigerated and then remained solid at ambient temperature. *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 ($CF(NO_2)_2$). Anal. Calcd: C, 26.53; H, 3.34; N, 15.47. Found: C, 26.76; H, 3.32; N, 14.70.

1-Bromo-4-(2-fluoro-2,2-dinitroethoxy)pentane (8). 1,4-Dibromopentane (8.04 g, 35.0 mmol) was added to a slurry of 9.00 g of AgOTf (35.0 mmol) in 50 mL of ethanol-free $CHCl_3$ at 0 °C in a 100-mL flask with stirring. After 1 min, 5.40 g of fluorodinitroethanol (35.0 mmol) was added. After 5 min more, 4.97 g of Na_2SO_4 (35.0 mmol) was added. The mixture was left at 0 °C for 6.5 h and then was left at ambient temperature overnight. The solution was filtered through a pad of alumina along with 100 mL of $CHCl_3$; this solution was washed twice with 100-mL portions of dilute aqueous sodium bisulfite and 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 ($CDCl_3$) δ 1.58 (d, CH_3), 1.96 (m, CH_2), 3.46 (t, CH_2Br), 5.09 (m, CH). Compound **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 (CH_2CH), 33.3 (CH_2CH_2Br), 34.3 (CH_2Br), 65.8 (d, OCH_2), 78.1 (CH), 120.6 (d, $CF(NO_2)_2$). Anal. Calcd: C, 27.74; H, 3.99; N, 9.24. Found: C, 28.03; H, 4.08; N, 9.14.

1,4-Bis(2-fluoro-2,2-dinitroethoxy)pentane (9). Compound **8** (0.758 g, 2.50 mmol) was added to a slurry of 0.642 g of AgOTf (2.50 mmol) in 5 mL of CCl_4 at room temperature with stirring in a 10-mL flask. After 30 min, 0.385 g of fluorodinitroethanol (2.50 mmol) and 0.173 g of 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 yielded pure **9** in overall 39% yield from **8**. Compound **9**: ^{1}H NMR ($CDCl_3$) δ 1.18 (d, CH_3), 1.56 (m, CH_2), 3.63 (3 H, m, CHO, CH_2O), 4.52 (d, OCH_2CF); ^{13}C NMR ($CDCl_3$) δ 19.1 (CH_3), 24.9 (CH_2CH_2O), 32.4 (CH_2CHO), 68.3 (d, OCH_2CF), 73.4 (CH_2CH_2O), 78.7 (CH), 120.7 (d, $CF(NO_2)_2$). Anal. Calcd: C, 28.73; H, 3.75; N, 14.89. Found: C, 29.04; H, 3.87; N, 14.28.

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 1 equiv 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 species 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.

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