Conversion of Olefins to Ditriflates by μ-Oxobis[(trifluoromethanesulfonato)(phenyl)iodine]

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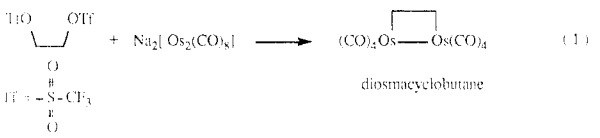
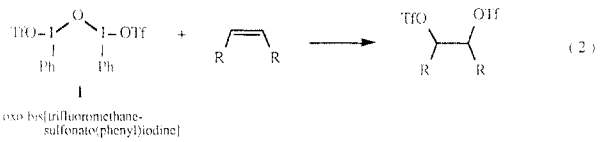
A new preparation of μ-oxobis[(trifluoromethanesulfonato)(phenyl)iodine], **1**, from iodosobenzene and triflic anhydride is reported. The use of **1** provides a mild, single-step procedure for the conversion of olefins to vicinal ditriflates and of dienes to 1,4-ditriflates. The reaction of **1** with cyclohexene and with *cis*- and *trans*-ethylene-*1,2-d*$_2$ results in syn addition. In the latter case, the $^3J_{HH}$ from the ^{13}C sidebands in the $\{^2H\}^1H$ NMR shows that the ditriflates from the use of **1** have the same stereochemistry as those prepared from *cis*- and *trans*-ethylene-*1,2-d*$_2$ via catalytic OsO_4 oxidation. The magnitudes of these coupling constants imply that the more stable rotamer of ethanediyl bis(trifluoromethanesulfonate) has gauche triflate groups.

Our interest in oberving the stereochemistry of the unusually facile evolution of ethylene from (μ-ethanediyl)-octacarbonyldiosmium,[1] a diosmacyclobutane, has required the preparation of stereochemically pure *meso*- and *dl*-ethanediyl-*1,2-d*$_2$ bis(trifluoromethanesulfonate). The unlabeled ditriflate is the preferred dielectrophile for the formation of the diosmacyclobutane (eq 1).



(1)

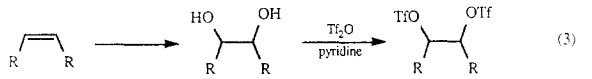
In recent years, several reports of the functionalization of olefins with hypervalent iodine species have appeared.[2,3] An interesting communication by Zefirov et al.[4] has reported that vicinal ditriflates are formed by the reaction of a reagent formulated as μ-oxobis[(trifluoromethanesulfonato)(phenyl)iodine], **1**, with olefins (eq 2).



1
μ-oxo bis[trifluoromethanesulfonato(phenyl)iodine]

(2)

Traditionally ditriflates have been prepared by the reaction of triflic anhydride with diols.[5] Preparation of the appropriately labeled and stereochemically pure ditriflates by this method requires a two-step approach. First, stereochemically pure *meso*- and *dl*-1,2-ethanediol-*1,2-d*$_2$ are prepared by the glycolization of *cis*- and *trans*-ethylene-*1,2-d*$_2$ using one of several methods of known stereochemistry.[6-11] Treatment of the diols with triflic anhydride yields the desired ditriflates without affecting the stereochemistry at carbon (eq 3). The stereochemistry of the glycolization is thus transferred to the ditriflate and provides the appropriate reference to establish the stereochemistry of the more convenient single-step preparation of the same labeled ditriflates using **1** (eq 2).

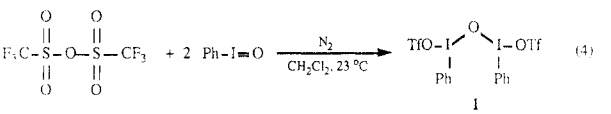


(3)

In this paper we report a modified preparation of **1**, its reaction with several olefins to form vicinal ditriflates, its 1,4-addition to butadiene, and the stereochemistry of its conversion of olefins to ditriflates.

Results and Discussion

Preparation of 1. Zefirov's reagent, **1**, is a μ-oxoiodine(III) species.[12] The reported method of preparing **1**, addition of HX (X = OSO_2CF_3) to iodobenzene diacetate, has been used in the preparation of several biscarboxylate analogues (X = CF_3CO_2, CCl_3CO_2, $ClCH_2CO_2$, $BrCH_2CO_2$);[13] however, in our hands this approach was not successful. We have found that **1** may be prepared and isolated as an insoluble yellow powder by the combination of 2 equiv of iodosobenzene with 1 equiv of triflic anhydride (eq 4).



1

(4)

We have found **1** to be a thermally stable compound that can be handled for brief periods in air and stored indefinitely under an atmosphere of N_2. Both the elemental analysis and its yellow color[14] support a μ-oxo dimeric structure for **1**. The μ-oxo functionality has recently been characterized in a crystal structure of the bis-trifluoroacetate analogue of **1**.[12]

(1) Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3468.

(2) [Hydroxy(tosyloxy)iodo]benzene reacts with olefins to yield ditosylates: (a) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 2462. (b) Shah, M.; Taschner, M. J.; Koser, G. F.; Rach, N. L. *Tetrahedron Lett.* **1986**, *27*, 4557. Iodine tris(trifluoroacetate) reacts with olefins to yield bis-trifluoroacetates: (c) Buddrus, J.; Plettenberg, H. *Chem. Ber.* **1980**, *113*, 1494.

(3) A recent review of the uses of polyvalent iodine species in organic synthesis discusses the reaction of many such species toward olefins: Varvoglis, A. *Synthesis* **1984**, 709.

(4) (a) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Y. V.; Kozmin, A. S. *J. Org. Chem. USSR (Engl. Transl.)* **1984**, *20*, 401; *Zh. Org. Khim.* **1984**, *20*, 446. (b) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Y. V.; Sorokin, V. D.; Semerikov, V. N.; Koz'min, A. S.; Caple, R.; Berglund, B. A. *Tetrahedron Lett.* **1986**, *27*, 3971. (c) Zefirov, N. S.; Koz'min, A. S. *Acc. Chem. Res.* **1985**, *18*, 154.

(5) (a) Lindner, E.; von Au, G.; Eberle, H.-J. *Chem. Ber.* **1981**, *114*, 810. (b) Lindner, E.; Schauss, E. *Chem. Ber.* **1985**, *118*, 4292.

(6) (a) Korach, M.; Nielsen, D. R.; Rideout, W. H. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 414. (b) Berti, G.; Macchia, B.; Macchia, F. *Tetrahedron Lett.* **1965**, 3421.

(7) Wilson, C. V. *Org. React. (N.Y.)* **1957**, *9*, 332.

(8) Woodward, R. B.; Brutcher, F. V., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 209.

(9) Schröder, M. *Chem. Rev.* **1980**, *80*, 187.

(10) Mangoni, L.; Matteo, A.; Barone, G.; Parrilli, M. *Gazz. Chim. Ital.* **1975**, *105*, 377.

(11) Cambie, R. C.; Rutledge, P. S. *Org. Synth.* **1980**, *59*, 169.

(12) A summary of the known μ-oxo-bridged iodine(III) species is included in: Gallos, J.; Varvoglis, A.; Alcock, N. W. *J. Chem. Soc., Perkin Trans. 1* **1985**, 757.

(13) Merkushev, E. B.; Novikov, A. N.; Kogai, T. I.; Glushkova, V. V. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 442; *Zh. Org. Khim.* **1972**, *8*, 436.

(14) The yellow color is considered characteristic of the bridging I–O–I group: Dasent, W. E.; Waddington, T. C. *J. Chem. Soc.* **1960**, 3350.

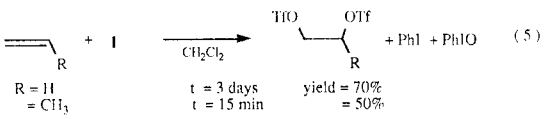
0022-3263/87/1952-3650$01.50/0

Table I. 1,4:1,2 Selectivity in Butadiene Functionalization

electrophile	X	1,4:1,2 selectivity	isolated yield (%)[a]	ref
1	OTf	89:11	55	this work
TeO_2/LiBr	OAc	91:9	17	*b*
SeO_2/LiBr/HoAc/Ac_2O	OAc	80:20	65	*c*
$Pd(OAc)_2$/LiOAcOAc	OAc	75:25	36	*d*
$Cu(OAc)_2$/LiBr/HoAc/Ac_2O	OAc	73:27	51	*c*
Br_2	Br	50:50	50	*e*
$Tl(OAc)_3$/AcOH	OAc	35:65	4	*f*
Cl_2	Cl	33:77	35	*g*

[a] Yield of 1,4-product isolated. [b] Uemura, S.; Miyoshi, H.; Tabata, A.; Okano, M. *Tetrahedron* **1981**, *37*, 291. [c] Stapp, P. R. *J. Org. Chem.* **1979**, *44*, 3216. [d] Reference 16. [e] Hatch, L. F.; Gardner, P. D.; Gilbert, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 5943. [f] Uemura, S.; Fukuzawa, S.; Okano, M. *Tetrahedron Lett.* **1981**, *22*, 5331. [g] Heasley, V. L.; Heasley, G. E.; Loghry, R. A.; McConnell, M. R. *J. Org. Chem.* **1972**, *37*, 2228.

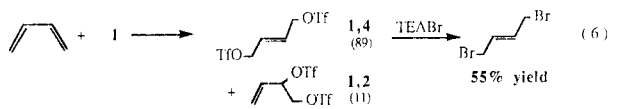
1,2 and 1,4 Additions with 1. A variety of reactions of hypervalent iodine species with alkenes are known.[3] We have observed **1** to react cleanly, although somewhat slowly, with ethylene and quite smoothly with propylene to give the appropriate 1,2-ditriflate in each case (eq 5).



(5)

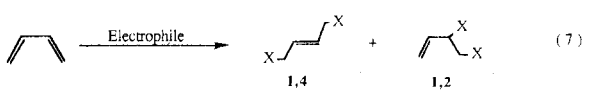
The byproducts of this reaction are **1** equiv each of iodobenzene and iodosobenzene. The former is observed in the ^1H NMR of the crude reaction products and the latter inferred from the appearance of a milky precipitate.[15] The isolated yields of the pure ethylene and propylene ditriflates were 70% and 50% respectively, thus providing ditriflates in one step from alkene in higher yield than the traditional two-step procedures.[6-11]

As recently pointed out by Bäckvall, methods that successfully functionalize alkenes in a 1,2 fashion often do not accomplish 1,4 addition to dienes.[16] Yet upon addition of 1 equiv of **1**, butadiene is consumed within minutes at 0 °C. ^{19}F NMR at this point indicates an 89:11 mixture of the 1,4:1,2 addition products. Although it has not yet been possible to isolate the bis-allylic ditriflate, addition of bromide converts the ditriflate to the dibromide, which is isolable as crystalline, white (*E*)-1,4-dibromo-2-butene without detectable contamination of the 1,2 addition product (eq 6).



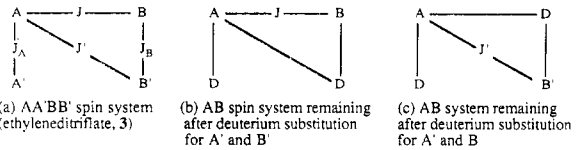
(6)

A survey of 1,4:1,2 selectivity in the reaction of butadiene with various electrophiles (eq 7) shows **1** to be a reagent capable of both high selectivity and good yield (Table I).



(7)

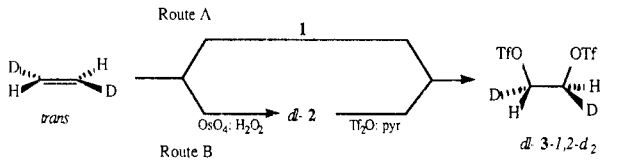
This result, along with the reported 1,4 reaction of [hydroxy(tosyloxy)iodo]benzene, Koser's reagent, with 2,4-hexadiene in 35% yield,[2a] suggests that hypervalent iodine reagents may be generally useful for such selective 1,4 functionalization.



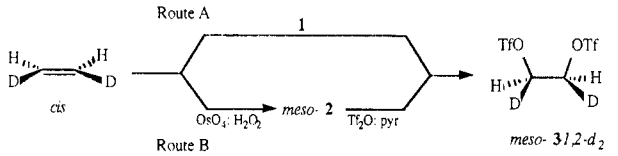
(a) AA'BB' spin system (ethyleneditriflate, **3**) (b) AB spin system remaining after deuterium substitution for A' and B' (c) AB system remaining after deuterium substitution for A' and B

Figure 1. AA'BB' spin system coupling constants.

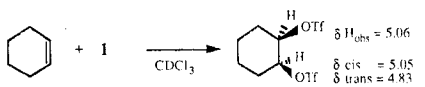
Scheme I



Scheme II



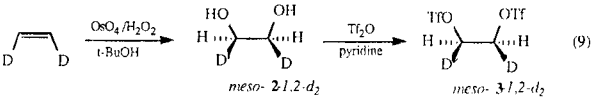
Stereochemistry of 1,2 Addition to Cyclohexene. The syn addition suggested by Zefirov[4] for the reaction of **1** with cyclohexene (eq 8) has been proven by comparison



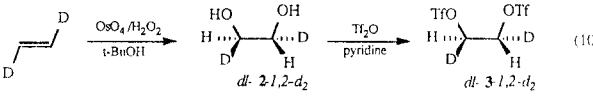
(8)

of the ^1H NMR spectrum of this product with those of the ditriflates independently prepared from *cis*- and *trans*-cyclohexanediols and triflic anhydride.[5] The results were unambiguous and consistent with >99% syn addition.

Preparation of 1,2-Ethanediol-*1,2-d*$_2$. Alkenes may be converted to glycols with stereochemical control by acid- or base-catalyzed epoxide opening,[6] the Prévost reaction,[7] the Woodward method,[8] and alkene glycolization by oxometal species.[9] Both epoxide opening and recent, more efficient variations of the Prévost[10] reaction and Woodward methods[11] require isolation of an intermediate product from alkene oxidation before hydrolysis to the glycol. We therefore chose catalytic osmium tetraoxide oxidation as a single-step procedure to the desired deuterium-labeled glycols.[17] This procedure yields *meso*-1,2-ethanediol-*1,2-d*$_2$, *meso*-**2**-*1,2-d*$_2$, from *cis*-ethylene-*1,2-d*$_2$ (eq 9) and



(9)



(10)

dl-1,2-ethanediol-*1,2-d*$_2$, *dl*-**2**-*1,2-d*$_2$, from *trans*-ethylene-*1,2-d*$_2$ (eq 10). These diols were then converted to the desired ditriflates *meso*- and *dl*-**3**-*1,2-d*$_2$ with triflic anhydride in pyridine,[5a] a process expected to occur without affecting the carbon stereochemistry.

Stereochemistry of 1,2 Addition to Ethylene. Reaction of Zefirov's reagent, **1**, with *cis*- and *trans*-ethylene-*1,2-d*$_2$ provided **3**-*1,2-d*$_2$ products (route A, Schemes I and II), which were compared spectroscopically with the samples of *meso*- and *dl*-**3**-*1,2-d*$_2$ prepared by the OsO_4/

(15) Iodosobenzene is known to have a polymeric structure: Siebert, H., Handrich, M. *Z. Anorg. Allg. Chem.* **1976**, *426*, 173.
(16) Bäckvall, J.-E.; Bystrom, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619.
(17) Milas, N. A.; Sussman, S. *J. Am. Chem. Soc.* **1937**, *59*, 2345.

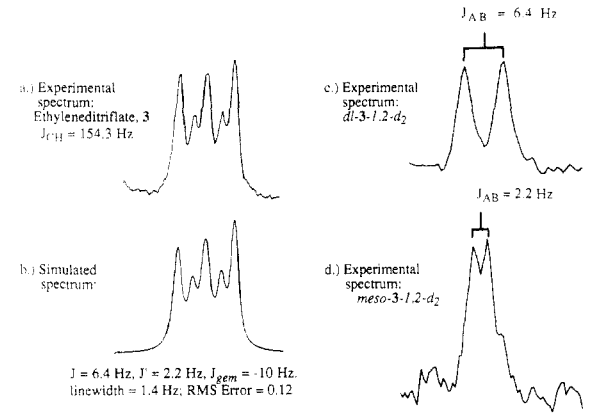


Figure 2. ^{13}C sidebands in the ^1H NMR of ethyleneditriflate (**3**), *meso*-**3**-*1,2*-d_2, and *dl*-**3**-*1,2*-d_2.

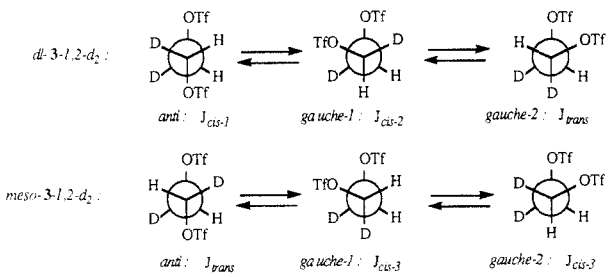


Figure 3. Rotational isomers of ethyleneditriflate-*1,2*-d_2 (*dl*-**3**-*1,2*-d_2 and *meso*-**3**-*1,2*-d_2) and their $^3J_{HH}$ coupling constants.

Tf_2O route described above (route B, Schemes I and II). Two separate NMR methods were employed in this comparison.

^{13}C Sideband Analysis. In symmetrically 1,2-disubstituted ethanes (XCH_2CH_2X) the ^1H NMR is normally that of a A_4 spin system. As demonstrated by Sheppard and Turner,[18] the incorporation of an unsymmetrically coupled ^{13}C nucleus into such a spin system transforms it to AA'BB'X ($J_{AX} = J_{A'X} \gg J_{BX} = J_{B'X}$). Therefore, the natural abundance ^{13}C sidebands in the ^1H NMR of such systems provide AA'BB' subspectra which may be analyzed to obtain the vicinal and geminal couplings defined in Figure 1a.[19] Spectral simulation of the ^{13}C sidebands of ethyleneditriflate determined the vicinal couplings J and J' to be 6.4 and 2.2 Hz, respectively (see Figures 2a and 2b).[20]

Substitution of two deuterium atoms into ethyleneditriflate, as in *meso*- and *dl*-**3**-*1,2*-d_2, selectively removes the geminal and one vicinal J_{HH} coupling in each case. With deuterium decoupling the ^{13}C sideband should be simplified and contain only J or J' (as diagrammed above in Figures 1b and 1c), identical with the values obtained from the above simulation.

J and J' are rotationally averaged values that depend on both the relative populations of rotamers with the triflate groups anti (n_a) and gauche (n_g) along with the static values of J_{HH} (J_{trans} or J_{cis}) present in each rotamer. As shown in Figure 3, although the gauche-1 and gauche-2 rotamers will be degenerate in energy, they may contain different contributions to J or J'. In *dl*-**3**-*1,2*-d_2 the gauche-1 rotamer contains the coupled protons synclinal with a J_{HH} designated J_{cis-2}, while the gauche-2 rotamer holds the coupled protons antiperiplanar with a J_{HH} designated J_{trans}.[21]

Equations 11 and 12 show in detail how these contributions are combined in the observed values of J and J'. Due to the presence of J_{trans} and J_{cis} couplings in both diastereomers, distinguishing *meso*- from *dl*-**3**-*1,2*-d_2 by this method requires the existence of a significantly different population of anti (n_a) and gauche (n_g) rotamers, otherwise the observed values of J and J' become composed of similar J_{trans} and J_{cis} contributions. For instance, if the anti rotamer is exclusively populated, $n_a = 1.0$, then in *meso*-**3**-*1,2*-d_2, $J'_{obs} = J_{trans}$, while in *dl*-**3**-*1,2*-d_2, $J_{obs} = J_{cis-1}$. The simulated values of $J = 6.4$ Hz and $J' = 2.2$ Hz demonstrate that this necessary unbalanced rotamer population does exist and that the $\{^2H\}^{13}C$ sidebands in the ^1H NMR spectrum may be used to distinguish *meso*- from *dl*-**3**-*1,2*-d_2.

$$dl\text{-}\mathbf{3}\text{-}1,2\text{-}d_2 \qquad J_{obs} = n_a J_{cis\text{-}1} + 0.5 n_g J_{cis\text{-}2} + 0.5 n_g J_{trans} \tag{11}$$

$$meso\text{-}\mathbf{3}\text{-}1,2\text{-}d_2 \qquad J'_{obs} = n_g J_{cis\text{-}3} + n_a J_{trans} \tag{12}$$

In agreement with the predicted values, the deuterium-decoupled ^1H NMR spectra of the products of bis-triflation of *trans*-ethylene-*1,2*-d_2 (route A and route B, Scheme I) show a clearly resolved doublet with $^3J_{HH} = 6.4$ Hz matching the simulated value of $J = 6.4$ Hz (Figure 2c). As reasoned above, this is assigned the *dl* configuration. The products of bis-triflation of *cis*-ethylene-*1,2*-d_2 (route A and B, Scheme II) show a doublet with $J = 2.2$ Hz in the deuterium-decoupled spectrum consistent with the expected value for $J' = 2.2$ Hz (Figure 2d). These products are assigned the *meso* configuration. Both results show the ditriflates obtained from OsO_4/Tf_2O route have identical stereochemistry with those obtained by the direct reaction of **1** with *cis*- and *trans*-ethylene-*1,2*-d_2, consistent with syn addition of the ditriflate functionality.

Liquid Crystal NMR. These conclusions were supported by a second method of testing the stereochemical purity of each diastereomer. All four **3**-*1,2*-d_2 species prepared in Schemes I and II above were converted to their corresponding deuterium-labeled diosmacyclobutanes, *cis*- and *trans*-**4**-*3,4*-d_2 (eq 13 and 14).

Analysis of the ^1H NMR of *cis*- and *trans*-**4**-*3,4*-d_2 in a nematic liquid crystal phase[1] provides unambiguous proof of both the relative stereochemistry and the stereochemical purity of each sample on the basis of the observed dipolar couplings $D_{trans} = \pm 520.2$ Hz and $D_{cis} = \pm 934.0$ Hz. Each sample was shown to be >95% stereochemically pure and in agreement with the absolute configuration assigned

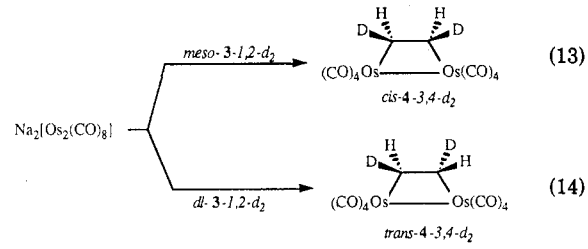
(18) (a) Cohen, A. D.; Sheppard, N.; Turner, J. J. *Proc. Chem. Soc., London* **1958**, 118. (b) Sheppard, N.; J. J. Turner *Proc. R. Soc. London, A A* **1959**, *252*, 506.

(19) (a) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; p 119. (b) Hoffman, R. A.; Forsén, S.; Gestblom, B. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1971; Vol. 5, p 106.

(20) The geminal couplings $J_A = J_B = -10$ Hz also emerge from this analysis, but as has been previously noted, the fit of the simulated spectrum is quite insensitive to variation ±2 Hz of this value. Zetta, L.; Gatti, G. *Tetrahedron* **1972**, *28*, 3773.

(21) As observed by Whitesides, the vicinal coupling between protons is most affected by the substituent in the trans position. Therefore, in the rotamers of *meso*- and *dl*-**3** three separate cis coupling constants should be present: in the *dl* isomer, J_{cis-1}, which has no triflate groups trans to coupled protons, and J_{cis-2}, which has two triflate groups trans to a coupled proton; in the meso isomer, J_{cis-3} (present in both gauche rotamers) which has one triflate group trans to a coupled proton. Whitesides, G. M.; Sevenair, J. P.; Goetz, R. W. *J. Am. Chem. Soc.* **1967**, *89*, 1135.

(22) We expect triflates to have steric properties similar to those of other sulfonate ester groups. Tosyl groups have steric effects on cyclohexane conformational equilibria similar to those of bromides and methyl groups. The steric repulsion of two methyl groups in a 1,2-disubstituted ethane causes the population of anti:gauche rotamers in *n*-butane to be about 2:1 at room temperature. Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Wiley-Interscience: New York, 1965; pp 438 and 11.



through the combination of chemical reasoning and ^{13}C sideband analysis above.

Rotamer Stability. The relative magnitudes of the J_{obs} and J'_{obs} assignments made above for the *dl*- and *meso*-**3**-*1,2-d*$_2$ diastereomers are surprising. If the anti rotamer of **3** were more stable, then a larger observed scalar coupling would be predicted for *meso*-**3**-*1,2-d*$_2$ as the coupled protons would be trans to each other in the anti rotamer. However, we observe a larger coupling for *dl*-**3**-*1,2-d*$_2$. The electronegativity of the triflate groups may be expected to cause a reduced value for both J_{trans} and J_{cis};[23] however, it is not expected to invert their relative magnitudes. The $\cos^2\theta$ dihedral angle dependence of the Karplus relationship for vicinal couplings requires $J_{trans} > J_{cis}$.[24] The observed scalar couplings imply that the gauche rotamers of the ditriflates are more stable than the anti. In this case, a larger value of J_{obs} for *dl*-**3** would be observed due to the dominant contribution of J_{trans} (see the gauche-2 rotamer of *dl*-**3** in Figure 3).

The preference of **3** for a gauche conformation is unexpected on steric grounds[22] but expected as an example of the gauche effect;[25] indirect evidence has been offered for a strong interaction between two tosylates,[25a] and an even stronger attractive interaction may be anticipated between two gauche triflates.

Experimental Section

Triflic anhydride,[26] iodobenzene diacetate,[27] iodosobenzene,[28] acetylene-*d*$_2$,[29] *cis*- and *trans*-ethylene-*1,2-d*$_2$,[29] and Ag-impregnated silica[30] were prepared by using standard procedures. 99% *cis*-Cyclohexane-1,2-diol was obtained from Polysciences, Warrington, PA. ^1H and ^{13}C NMR spectra were collected on an IBM WP-270SY spectrometer. ^{19}F NMR spectra were collected on an IBM WP-200SY. Broadband $\{^2H\}^1H$ NMR spectra were collected on a Nicolet NT-360 with a decoupling power of 1-5W at 55.27 MHz. Solvents were freshly distilled from P_2O_5 before use. Solutions were degassed as indicated by freezing at −196 °C, evacuating, and thawing three times.

μ-Oxobis[(trifluoromethanesulfonato)(phenyl)iodine], 1. Triflic anhydride (1.17 g, 4.14 mmol) in CH_2Cl_2 (5 mL) was added slowly at room temperature to a stirred mixture of freshly prepared and carefully dried iodosobenzene (1.77 g, 8.05 mmol) in 5 mL of CH_2Cl_2 in a flame-dried 50-mL three-neck flask under a N_2 atmosphere. The solution became homogeneous and lemon yellow after 5 min, and after another 20 min a yellow solid precipitated from solution. This solid was collected on a Schlenk filter under a N_2 atmosphere, rinsed with 3 × 5 mL portions of CH_2Cl_2, and dried overnight at room temperature under dynamic vacuum. The yellow powder, 2.68 g (93% yield), was placed in a storage vial under N_2. The yellow solid is mildly air-sensitive but thermally stable and may be stored for months under an atmosphere of N_2. ^1H NMR (CD_3CN): δ 8.06 (m, 2 H), 7.72 (m, 1 H), 7.51 (m, 2 H). $\{^1H\}^{13}C$ NMR (CD_3CN): δ 137.4, 136.1, 133.5, 125.3, 120.8 (J_{CF} = 319.2 Hz). ^{19}F NMR (CD_3CN): δ −45.8 (rel to $CFCl_3$). Anal. Calcd for $C_{14}H_{10}O_7F_6S_2I_2$: C, 23.26; H, 1.40; F, 15.79; I, 35.15; S, 8.89. Found: C, 23.16; H, 1.45; F, 15.65; I, 35.15; S, 8.64.

1 + Cyclohexene. Cyclohexene (0.016 mmol) was vacuum transferred to a 5-mm NMR tube containing **1** (9.0 mg, 0.012 mmol) and $CDCl_3$ (0.5 mL). The mixture was degassed, sealed under vacuum, and thawed to room temperature. The ^1H NMR showed complete consumption of the cyclohexene and formation of both iodobenzene and *cis*-1,2-cyclohexaneditriflate. Identification of the latter was made by spectral comparison with the ^1H NMR spectrum of independently prepared *cis*- and *trans*-1,2-cyclohexaneditriflates as described below.

***cis*-1,2-Cyclohexanediyl 1,2-bis(trifluoromethanesulfonate)** was prepared by the procedure of Lindner et al[5a] and recrystallized from pentane at 0 °C in an isolated yield of 16%. ^1H NMR ($CDCl_3$): δ 5.06 (m, 2 H), 2.39 (m, 2 H), 1.87 (m, 4 H), 1.42 (m, 2 H). ^{19}F NMR ($CDCl_3$): δ −40.80 (rel to $CFCl_3$). Anal. Calcd for $C_8H_{10}O_6F_6S_2$: C, 25.26; H, 2.65. Found: C, 25.29; H, 2.67.

***trans*-1,2-Cyclohexanediyl bis(trifluoromethanesulfonate)** was prepared as the cis isomer above in 34% isolated yield. ^1H NMR ($CDCl_3$): δ 4.83 (m, 2 H), 2.42 (m, 2 H), 1.82 (m, 4 H), 1.41 (m, 2 H). ^{19}F NMR ($CDCl_3$): δ −40.98 (rel to $CFCl_3$). Anal. Calcd for $C_8H_{10}O_6F_6S_2$: C, 25.26; H, 2.65. Found: C, 25.27; H, 2.58.

1 + Ethylene. In a flame-dried 30-mL standard reaction bulb were placed 227 mg of **1** (.31 mmol) and CH_2Cl_2 (8 mL). After degassing on vacuum line, ethylene (0.31 mmol) was condensed into the bulb and stirred at room temperature. After 64 h the mixture became homogenous and after another 24 h it grew cloudy as a white precipitate formed. The solution was concentrated to about 3 mL and filtered through a plug of Ag-impregnated silica. The solvent was then removed under reduced pressure to yield a white solid, 71 mg (70% yield) spectroscopically pure ethyleneditriflate: ^1H NMR ($CDCl_3$): δ 4.78 (J_{CH} = 154.3 Hz). $\{^1H\}^{13}C$ NMR ($CDCl_3$): δ 119.1 (J_{CF} = 319.7 Hz), 72.5. ^{19}F ($CDCl_3$): δ −41.4 (s) (rel to $CFCl_3$).

1 + *cis*-Ethylene-*1,2-d*$_2$. *cis*-Ethylene-*1,2-d*$_2$ (0.86 mmol) was reacted with **1** (652 mg, 0.90 mmol) and the product ethaneditriflate-*d*$_2$ isolated as above.

1 + *trans*-Ethylene-*1,2-d*$_2$. *trans*-Ethylene-*1,2-d*$_2$ (0.86 mmol) was reacted with **1** (651 mg, 0.90 mmol) and the product ethaneditriflate-*d*$_2$ isolated as above.

***dl*-1,2-Ethanediol-*1,2-d*$_2$, *dl*-2-*1,2-d*$_2$.** Aqueous H_2O_2 (13.4 mL, 30 wt %), OsO_4 (2.0 mL, 4 wt % in water), and 25 mL of *tert*-butyl alcohol were placed in a 100-mL flask. After degassing an atmosphere of *trans*-ethylene-*1,2-d*$_2$ (700 Torr, 25 mmol) was placed over the stirred solution at 23 °C for 168 h. Following the removal of *tert*-butyl alcohol under reduced pressure and azeotropic removal of the benzene, the product, 65.8 mg (4% yield), was collected by Kügelrohr distillation at 85–95 °C at 13 mmHg. ^{1}NMR (acetone-*d*$_6$): δ 3.51 (s, 2 H), 3.6 (OH).

***meso*-1,2-Ethanediol-*1,2-d*$_2$, *meso*-2-*1,2-d*$_2$.** Using the same procedure as above *cis*-ethylene-*1,2-d*$_2$ (10.9 mmol) gave 83.0 mg (11% yield) of distilled product. ^{1}NMR (acetone-*d*$_6$): δ 3.51 (s, 2 H), 3.6 (OH).

***dl*-Ethanediyl-*1,2-d*$_2$ bis(trifluoromethanesulfonate), *dl*-3-*1,2-d*$_2$,** was prepared by the method of Lindner et al[5a] using *dl*-1,2-ethanediol-*1,2-d*$_2$. A solution of *dl*-**3**, 9.6 wt % in CD_2Cl_2, was used for the $\{^2H\}^1H$ NMR.

***meso*-Ethanediyl-*1,2-d*$_2$ bis(trifluoromethanesulfonate), *meso*-3-*1,2-d*$_2$,** was prepared by the method of Lindner et al[5a] using *meso*-1,2-ethanediol-*1,2-d*$_2$. A solution of *meso*-**3**, 12.3 wt % in CD_2Cl_2, was used for the $\{^2H\}^1H$ NMR.

1 + Propylene. A CH_2Cl_2 suspension of **1** (270 mg, 0.37 mmol) was treated with propylene (0.37 mmol) as in the reaction with ethylene above. Within 5 min of thawing to room temperature and stirring, 1 had dissolved and the solution became homogeneous. After 30 min a precipitate formed. After 1 h the solution

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was filtered three times through a plug of Ag-impregnated silica to remove the C_6H_5I. The yield of spectroscopically pure 1,2-propaneditriflate was 123 mg (50%). ^1H NMR ($CDCl_3$): δ 5.21 (m, 1 H), 4.56 (m, 2 H), 1.59 (d, J = 11.4 Hz). $\{^1H\}^{13}C$ ($CDCl_3$): δ 81.5, 74.9, 17.1. ^{19}F ($CDCl_3$): δ -40.7 (s), -41.4 (s) (rel to $CFCl_3$).

1 + Butadiene. A suspension of 1 (280 mg, 0.39 mmol) in 25 mL of CH_2Cl_2 was prepared in a flame-dried 50-mL Schlenk flask under N_2. As above, butadiene (0.380 mmol) was condensed into the Schlenk flask and thawed at 0 °C. Within a couple of minutes 1 dissolved and the mixture became homogeneous. $[Et_4N]Br$ (240 mg, 1.14 mmol) in 5 mL of CH_2Cl_2 was added via syringe under N_2 flow. The solution was stirred for an additional 3 h at 0 °C and filtered; after its volume was reduced to 2 mL, it was spotted on a Chromatotron plate and eluted with 15% CH_2Cl_2/hexane. Iodobenzene (R_f 0.50) and 1.4-dibromo-2-butene (R_f 0.35) were separated, yielding 45 mg (55% yield) of white crystalline 1,4-dibromo-2-butene.

1 + Butadiene. Butadiene (.023 mmol) was condensed into a 5-mm NMR tube containing 1 (17 mg, 0.023 mmol) and $CDCl_3$ (.35 mL), degassed, and sealed. After the tube was warmed to room temperature, ^1H NMR showed two strong bands at δ 6.09 and 5.02 along with iodobenzene and a trace of butadiene remaining. An ^{19}F NMR of this sample shows three absorptions at δ -41.15 (0.06), -41.24 (1.00), and -41.71 (0.06) (intensities in parentheses). Attempts to concentrate the products for isolation led to decomposition to a brown residue.

NMR Spectral Simulation. A computer program provided by IBM Instruments, Inc., known as parameter adjustment in NMR by iteration calculation (PANIC), was used for spectral simulation on an Aspect 2000 computer. Initial estimated chemical shifts and coupling constants are incorporated to calculate a spectrum, which is compared to the experimental one. An iteration process is then performed until the differences between the two are minimized.

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Registry No. 1, 88016-29-9; *dl*-**2**-*1,2-d*$_2$, 108868-25-3; *meso*-**2**-*1,2-d*$_2$, 108868-26-4; *dl*-**3**-*1,2-d*$_2$, 108868-27-5; *meso*-**3**-*1,2-d*$_2$, 108149-56-0; $CF_3SO_2O(CH_2)_2OSO_2CF_3$, 18928-34-2; *cis*-CHD=CHD, 2813-62-9; *trans*-CHD=CHD, 1517-53-9; triflic anhydride, 358-23-6; iodosobenzene, 536-80-1; cyclohexene, 110-83-8; *cis*-1,2-cyclohexanediol bis(trifluoromethanesulfonate), 91146-10-0; (±)-*trans*-1,2-cyclohexanediol bis(trifluoromethanesulfonate), 108868-24-2; ethylene, 74-85-1; 1,2-propanediol ditriflate, 108868-28-6; 1,3-butadiene, 106-99-0; (*E*)-1,4-dibromo-2-butene, 821-06-7; propylene, 115-07-1.

Pyridoxal-Mediated Dephosphonylation of 1-Amino Phosphonic Acids

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The reaction between pyridoxal and α-amino phosphonic acids is reported. Under the proper conditions, the amino phosphonates can be induced to undergo a pyridoxal-promoted cleavage of the P–C bond. The reaction requires a metal ion and a phosphonic acid that possesses a chelating heteroatom in a position β to the amino group. At 100 °C and pH 8.8, the dephosphonylation reaction is a first-order process, producing orthophosphate and an aldehyde from the amino phosphonate and pyridoxamine from the pyridoxal. The mechanism proposed for this reaction is based on an analogy with the pyridoxal-catalyzed decarboxylation of α-amino acids. The reactions reported represent the first observation of an α dephosphonylation mediated by pyridoxal.

A wide variety of phosphonic acids are known that have extremely potent biological activity. Glyphosate is one particularly well-known example in the herbicide field.[1] Of increasing interest are α-amino phosphonate analogues of natural amino acids.[2] When incorported into the proper polypeptide sequence, these analogues have proven to be extremely effective inhibitors of various serine proteases. The stability of the P–C bond in these molecules raises questions about possible mechanisms for the biodegradation of amino phosphonates. The chemistry of the P–C bond precludes nucleophilic attack at the phosphorus or carbon atom as a viable mechanism for the cleavage of this bond. To date, only a few specific examples of enzymatic reactions leading to cleavage of a P–C bond are known. Recently, Cordiero et al.[3] reported the metabolism of alkane- and alkenephosphonic acids by *Escherichia coli*. Incubation of methanephosphonate with the bacteria resulted in the formation of methane and orthophosphate, for example. These products suggest the formation of a phosphinyl radical anion as an intermediate. The P–C bond cleaves homolytically, producing monomeric metaphosphate anion and a methyl radical. The carbon radical subsequently abstracts a hydrogen atom to form methane, while the metaphosphate reacts with water to form the orthophosphate.

The mechanism for the biodegradation of phosphonoacetylaldehyde was elucidated by La Nauze[4]. The reaction is enzyme catalyzed and involves the initial formation of a Schiff base between the aldehyde carbonyl carbon and

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