$$k_\psi = k_M[R^+O^-]/([R^+O^-] + [R^+OH]) \qquad (3)$$

The values of k_ψ were for 5×10^{-4} M **3** in 0.001 M NaOH, and 10^{-3} M **3** in 0.01 M NaOH, and from an apparent pK_b = 1.7 for micellized **3** values of $[R^+O^-]/([R^+O^-] + [R^+OH])$ are 0.05 and 0.33, respectively, which gives $10^3k_M = 3.6$ and 3.3 s^{-1}, respectively, for reaction with the alkoxide derivative of **3**.

A similar calculation can be made for reaction with **1** in H_2O:MeCN (80:20, v/v) where we assume that the value of $k_\psi \approx 2.5 \times 10^{-4}$ s^{-1} corresponds to reaction of fully bound substrate (Table II). In this solvent pK_b = 0.8(app) so that application of eq 2 gives $k_M \approx 4 \times 10^{-3}$ s^{-1} for reaction of **2** and 0.01 M NaOH.

These comparisons show that k_M is very similar in the aqueous micelles of **3** and in the nonmicellizing hydrophobic ammonium ion (**1**) in H_2O:MeCN (80:20 v/v), despite the difference in solvent composition. Similar values of k_M have been found for reactions in micelles and in hydrophobic ammonium ions.[14]

The second-order rate constants k_M, s^{-1}, cannot be compared directly with second-order rate constants k_W, M^{-1} s^{-1}, in water because of the difference in dimensions.[8,25] The concentration expressed as mole ratio can be converted into molarity in the micellar pseudophase, assuming that reaction occurs in the micellar Stern layer whose assumed molar volume is 0.14 L.[26] The second-order rate constant k_2^m, M^{-1} s^{-1}, is given by[8,25] (eq 4) and values of k_2^m can be compared with those of k_W in water.

$$k_2^m = 0.14k_M \qquad (4)$$

For reaction of bis-2,4-DNPP in micelles of **3**, $k_M \approx 3.5 \times 10^{-3}$ s^{-1} and $k_2^m \approx 5 \times 10^{-4}$ M^{-1} s^{-1}. The second-order rate constant for reaction of cholinate zwitterion in water is 4.7×10^{-3} M^{-1} s^{-1}, neglecting the salt effect of choline chloride. The second-order rate constant for reaction of OH^- with bis-2,4-DNPP in water is ca. 3×10^{-3} M^{-1} s^{-1},[2] so that the second-order rate constant for reaction of bis-2,4-DNPP with the alkoxide moiety in micelles of **4** is somewhat lower than the second-order rate constants for reactions of hydroxide ion and cholinate zwitterion in water.[28] In dephosphorylations of *p*-nitrophenyl diphenyl phosphate in cationic micelles nucleophilicity in the micellar pseudophase is typically similar to but lower than that in water.[15a,29] The overall rate enhancement in these and other bimolecular reactions mediated by colloidal aggregates is generally due to the bringing together of the reagents, rather than to enhanced reactivity of the nucleophile, for example. In reactions of monoanionic bis-2,4-DNPP substrate binding to the cationic aggregate is strengthened by coulombic attractions.

Experimental Section

Materials. Bis(2,4-dinitrophenyl) phosphate was prepared as the pyridine salt, mp 157-158 °C (lit. mp 156-157 °C).[2] Preparation of the ammonium salts has been described,[14] and purification of the other reagents was by standard methods.

Kinetics. Formation of 2,4-dinitrophenoxide ion was followed spectrophotometrically at 25.0 °C in Gilford or Beckman spectrophotometers with 7×10^{-6} M substrate. The integrated first-order rate constants k_ψ are in reciprocal seconds.

Reaction Products. Reaction of bis-2,4-DNPP in solutions of **1** in H_2O:MeCN (90:10 and 80:20, v/v) and 0.001–0.01 M NaOH gave release of equimolar 2,4-dinitrophenoxide ion, and the second mole of phenoxide ion was released slowly.

Reaction of 5×10^{-4} M bis-2,4-DNPP in aqueous 0.08 M **3** and 10^{-3} M NaOH also gave release of equimolar 2,4-dinitrophenoxide ion. The cationic surfactant plus its phosphorylated derivative was precipitated by addition of $NaClO_4$. The precipitate was washed (H_2O) and then dissolved in EtOH. This solution absorbed at 290 nm (shoulder) but not in the visible region. The second mole of phenoxide ion was released quantitatively over a period of several days after addition of 0.1 M NaOH.

Acknowledgment. Support of this work by the U.S. Army Office of Research is gratefully acknowledged.

Registry No. 1, 92642-02-9; 2, 92642-03-0; 3, 20917-32-2; 4, 93254-09-2; choline chloride, 67-48-1.

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[25] Bunton, C. A.; Carrasco, N.; Huang, S. K.; Paik, C. H.; Romsted, L. S. *J. Am. Chem. Soc.* **1978**, *100*, 5420.

[26] A larger volume element of reaction is sometimes assumed which leads to a larger value of k_2^m, but the various estimates are within a factor of approximately 2.[7b,27]

[27] Martinek, K.; Yatsimirski, A. K.; Levashov, A. V.; Berezin, I. V. In ref 23, p 489. Chaimovich, H.; Aleixo, R. M. V.; Cuccovia, I. M.; Zanette, D.; Quina, F. H. In ref 7c, p 949.

[28] Our estimated second-order rate constant for reaction of cholinate zwitterion in water may be too low, because cholinate is generally a better nucleophile than OH^-. The underestimation is probably due to a negative salt effect of choline chloride.

[29] Bunton, C. A. *Pure Appl. Chem.* **1977**, *49*, 969.

Fluorination of 1,3-Dienes with Xenon Difluoride and (Difluoroiodo)Benzene

Dale F. Shellhamer,* R. Jeffrey Conner,
Ruthann E. Richardson, and Victor L. Heasley

Department of Chemistry, Point Loma College, San Diego, California 92106

Gene E. Heasley

Department of Chemistry, Bethany Nazarene College, Bethany, Oklahoma 73008

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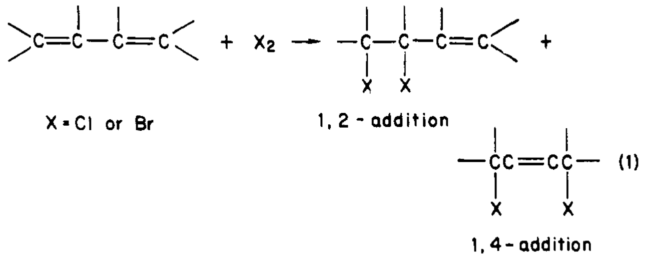
Ionic fluorinations of alkenes with xenon difluoride (XeF_2)[1a] and (difluoroiodo)benzene ($C_6H_5IF_2$)[2] have previously been reported. More recently, Shackelford[1b] described the photochemical reaction and we[1c] reported on the photochemical and molecule-induced homolysis reactions of XeF_2 with alkenes. In this study we report on the ionic reaction[3] of XeF_2 anddC$_6$H$_5$IF$_2$ with butadiene (**1**), 2,3-dimethyl-1,3-butadiene (**2**), and *cis*- and *trans*-1,3-pentadiene (**3c** and **3t**). This report presents the first fluorination of a 1,3-diene.

Halogenation of 1,3-dienes gives both 1,2- and 1,4-addition products (eq 1). Reactions of bromine (and to a



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[1] (a) Filler, R. *Isr. J. Chem.* **1979**, *17*, 71–79. Shackelford, S. A. *J. Org. Chem.* **1979**, *44*, 3485. Gregorcic, A.; Zupan, M. *Ibid.* **1979**, *44*, 4120, 1255, and references therein. (b) Hildreth, R. A.; Druelinger, M. L.; Shackelford, S. A. *Tetrahedron Lett.* **1982**, *23*, 1159. (c) Shellhamer, D. F.; Ragains, M. L.; Gipe, B. T.; Heasley, V. L.; Heasley, G. E. *J. Fluorine Chem.* **1982**, *20*, 13.

[2] Patrick, T. B.; Scheibel, J. J.; Hall, W. E.; Lee, Y. H. *J. Org. Chem.* **1980**, *45*, 4492. Carpenter, W. *Ibid.* **1966**, *31*, 2688. Garvey, B. S.; Halley, L. F.; Allen, C. F. *J. Am. Chem. Soc.* **1937**, *59*, 1827. Dimroth, O.; Bockemueller, W. *Chem. Ber.* **1931**, *64*, 522.

[3] One reviewer suggested that we include a discussion of a radical cation. A radical cation mechanism has been reported for the XeF_2 reactions with aromatics by Filler.[1a] Zupan suggests, but gives no evidence for, an ion radical intermediate on the reaction pathway for reaction of XeF_2 with alkenes [Zupan, M.; Pollak, A. *J. Org. Chem.* **1977**, *42*, 1559). A radical cation mechanism seems quite possible, but our data does not discriminate between an ionic or radical cation pathway.

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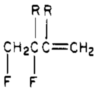
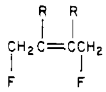
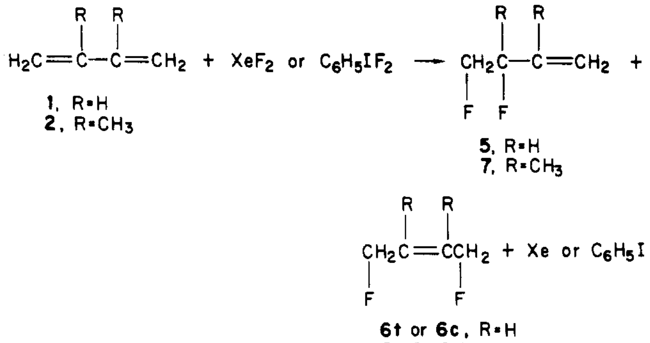
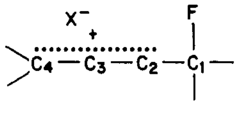
Table I. Halogenation of Butadiene (1) and 2,3-Dimethyl-1,3-butadiene (2)

			product ratio	
diene	electrophile	reactn condn (°C)	 $\underset{F}{CH_2}\overset{R}{\underset{F}{C}}\overset{R}{C}{=}CH_2$	 $\underset{F}{CH_2}\overset{R}{C}{=}\overset{R}{C}\underset{F}{CH_2}$
1, R = H	XeF_2	CH_2Cl_2 (-10)	87	13
1, R = H	XeF_2	CH_2ClCH_2Cl (-10)	75	25
1, R = H	$C_6H_5IF_2$	CH_2Cl_2 (0)	36	64
2, R = CH_3	XeF_2	CH_2Cl_2 (25)	100	
2, R = CH_3	$C_6H_5IF_2$	CH_2Cl_2 (0)	33	67

Scheme I



lesser extent chlorine) with dienes give a weakly bridged halonium ion intermediate.[4–6] Fluorination of a diene is expected to proceed through an open-ion intermediate (4).[7]



4

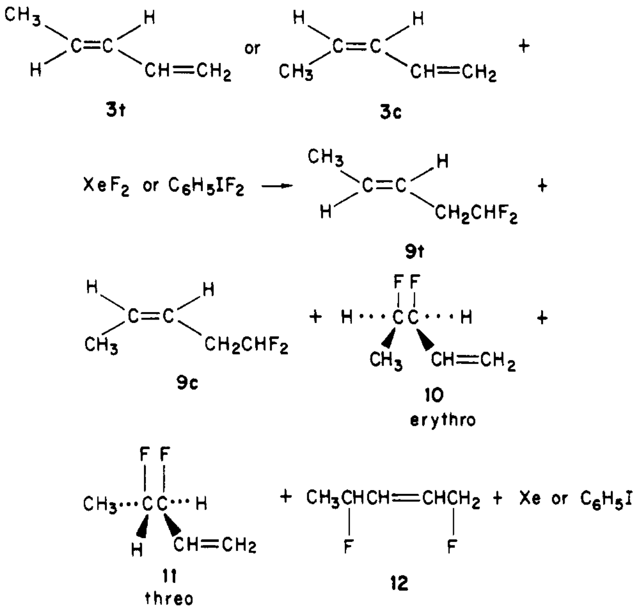
X = F or C_6H_5IF

Our goal was to examine the product distributions along with the stereochemistry for ionic fluorination of dienes 1, 2, 3c, and 3t with XeF_2 and $C_6H_5IF_2$.

Results

Reaction of XeF_2 or $C_6H_5IF_2$ with dienes gave 1,2- and 1,4-difluoro products. The products listed in Table I represent kinetic distributions from dienes 1 and 2 except for 8 which rearranges to 7 (Scheme I). Compound 8 could not be isolated. The remaining products were obtained pure by preparative vapor-phase chromatography (VPC). Structures were assigned on the basis of their spectral data. The cis and trans isomers 6c and 6t were synthesized independently from the dichlorides as described by Pattison.[8] This method could not be used to prepare other products insce elimination of hydrogen fluoride occured.

Scheme II



Reaction of XeF_2 or C_6H_5IF with 3c and 3t gave products resulting from addition across the 1,2- and 3,4-bonds of 3c and 3t (Table II), Scheme II). The erythro (10) and threo (11) products rearranged to 12, and the diallylic 1,4-product (12) polymerized on standing. These products were stable to the reaction and analysis conditions. The stereo- and regiochemistry of the products from 3c and 3t were determined by their NMR spectra.

Discussion

The product distributions for fluorination of dienes 1 and 2 are shown in Table I, and the data for fluorination of 3c and 3t are shown in Table II. Fluorination of the 1,3-dienes with XeF_2 gives primarily 1,2-products, while reaction of the same dienes with $C_6H_5IF_2$ gives significantly more of the 1,4-products. We suggest that the difference in product distribution may be due to the steric effect of the anion.[9,10] A steric interaction by the large anion ($C_6H_4IF^-$) would favor attact at the less-hindered number 4 carbon of intermediate 4.

Regio- and stereochemical data were obtained from fluorination of 3c and 3t. The data in Table II show that addition of fluorine to the 1,2-bond of 3c or 3t gives only the trans product 9t. This is in contrast to chlorination or bromination which occurs without isomerization of the disubstituted double bond (Table II). Thus, fluorination of 1,3-dienes proceeds through an allyl ion intermediate (4), while weakly bridged halonium ions are encountered for chlorination[4a,c] and bromination[4a,5c] of dienes.

We suggest that 9t results from rearrangement of the allyl cation intermediate as described below.[11] Control

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(4) (a) For the chlorination of 1, see: Heasley, V. L.; Heasley, G. E.; Loghry, R. A.; McConnell, M. R. *J. Org. Chem.* **1972**, *37*, 2228. (b) Chlorination of 2: Said, E. Z.; Tipping, A. E. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1986. (c) Chlorination of 3c and 3t: Heasley, G. E.; Hayse, D. C.; McClung, G. R.; Strickland, D. K.; Heasley, V. L.; Davis, P. D.; Ingle, D. M.; Rold, K. D.; Ungermann, T. S. *J. Org. Chem.* **1976**, *41*, 334.

(5) (a) For the bromination of 1, see ref 3a. (b) Bromination of 2: Said, E. Z.; Tipping, A. E. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1399. (c) Bromination of 3c and 3t: Heasley, V. L.; Heasley, G. E.; Taylor, S. K.; Frye, C. L. *J. Org. Chem.* **1970**, *35*, 2967.

(6) (a) Heasley, V. L.; Griffith, C. N. *J. Org. Chem.* **1975**, *40*, 1358. (b) Heasley, G. E.; McCully, V. M.; Wiegman, R. T.; Heasley, V. L.; Skidgel, R. A. *Ibid.* **1976**, *41*, 644. Heasley, G. E.; Emery, W. E., III; Hinton, R. A.; Shellhamer, D. F.; Heasley, V. L.; Rogers, S. L. *Ibid.* **1978**, *43*, 361.

(7) There is no evidence to support formation of fluoronium ions in solution; see: Olah, G. A.; Prakash, G. K. S.; Krishnamurthy, V. V. *J. Org. Chem.* **1983**, *48*, 5116.

(8) Pattison, F. L. M.; Norman, J. J. *J. Am. Chem. Soc.* **1957**, *79*, 2311.

(9) The bulky anion ($C_6H_5ICl^-$) was reported as an intermediate in the reactions of (dichloroiodo)benzene with unsaturated hydrocarbons; see: Heasley, V. L.; Rold, K. D.; McKee, D. B.; Heasley, G. E. *J. Org. Chem.* **1976**, *41*, 1287.

(10) A reviewer suggested that Xe^+F or ^+FIPh rather than XeF_2 or $PhIF_2$ may be the electrophilic species. Our data does not address this question. The reaction pathway might also be represented by a nucleophilic attack of the diene onto the neutral XeF_2 molecule to displace XeF^-.

(11) Formation of 1,1-difluoro products is not uncommon when alkenes are fluorinated which do not contain a phenyl ring in conjugation with the double bond (see ref 1b). We were surprised to find products 9c and 9t because dienes 1 and 2 did not give 1,1-difluoro products. Also, addition to the number 4 carbon of 3c or 3t does not give 4,4-difluoro-1-pentene.

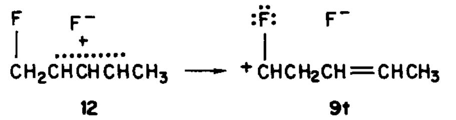
Table II. Halogenation of 1,3-Pentadienes 3c and 3t

diene	electrophile	reactn condn (°C)	X	product ratio				
				$CH_3CH{=}CHCH_2CHX_2$		$CH_3\underset{X}{CH}\underset{X}{CH}CH{=}CH_2$		$CH_3\underset{X}{CH}CH{=}CH\underset{X}{CH_2}$
				trans	cis	erythro	threo	
3c	XeF_2	CH_2Cl_2 (25)	F	76		4	18	2
3t	XeF_2	CH_2Cl_2 (25)	F	61		3	29	7
3c	$C_6H_5IF_2$	CH_2Cl_2 (25)	F	67		0.2	5	27
3t	$C_6H_5IF_2$	CH_2Cl_2 (25)	F	67		0.8	14	18

diene	electrophile	reactn condn (°C)	X	product ratio				
				$CH_3CH{=}CH\underset{X}{CH}\underset{X}{CH_2}$		$CH_3\underset{X}{CH}\underset{X}{CH}CH{=}CH_2$		$CH_3\underset{X}{CH}CH{=}CH\underset{X}{CH_2}$
				trans	cis	erythro	threo	
3c	Cl_2[a]	CH_2Cl_2 (−10)	Cl		47		10	43
3t	Cl_2[a]	CH_2Cl_2 (−10)	Cl	66		2		32
3c	Br_2[b]	CCl_4 (−15)	Br		31		13	56
3t	Br_2[b]	CCl_4 (−15)	Br	35		0.5		64.5

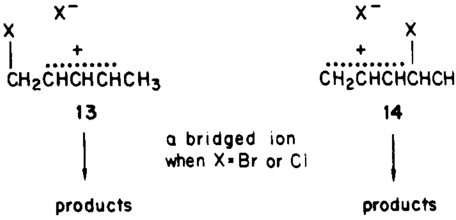
[a] See ref 4c. [b] See ref 5c.

experiments indicate that under the reactions conditions **9t** is produced kinetically and not from subsequent rearrangement of products **10**, **11**, or **12**.


$$\overset{F}{CH_2}\overset{F^-}{\overset{+}{CHCHCH}}CH_3 \longrightarrow {}^+\overset{:\ddot{F}:\quad F^-}{CH}CH_2CH{=}CHCH_3$$

Further support for intermediate **4** was obtained by comparison of the stereochemistry for addition to the disubstituted 3,4-bond of **3c** and **3t**. Chlorination and bromination are stereospecific at the internal bond of **3c** or **3t** (Table II). However, fluorination with either XeF_2 or $C_6H_5IF_2$ is stereoselective in that the threo isomer **11** is always preferred. These data are consistent with an open-ion intermediate as indicated by **4**.

The relative nucleophilicity of the 1,2- vs. 3,4-bond of 1,3-pentadiene can be obtained by comparing the kinetic product distribution for addition of these electrophiles to **3c** and **3t**. For example, electrophilic addition to the 1,2-bond gives a disubstituted allyl cation **13**, while initial addition to the 3,4-bond gives a monsubstituted allyl cation **14**. Caution must be exercised in the interpretation of these data because the same 1,4-product is produced by addition to either bond of 1,3-pentadiene. The data in Table II indicate that addition to the 1,2-bond of **3c** or **3t** is preferred for reaction of chlorine and bromine and for fluorination with XeF_2 and $C_6H_5IF_2$. We suggest that the kinetic transition state for electrophilic additions to 1,3-dienes has significant charge delocalization into the adjacent double bond. Kinetic studies indicate that even the transition state for addition of sulfenyl halides to 1,3-dienes has some charge delocalization into the adjacent π-bond.[12] This charge distribution in the kinetic transition state leads to a lower energy activated complex for formation of intermediate **13** over **14**. Thus addition to the 1,2-bond of **3c** or **3t** is preferred.



The mild reaction conditions for fluorination of unsaturated hydrocarbons with XeF_2 and $C_6H_5IF_2$ are indicated by the kinetic product distributions and the isolation of these rather unstable allylic and diallylic products.

Experimental Section

Butadiene was purchased from Matheson Gas Company, and the xenon difluoride was obtained from the PCR Research Chemical Company. All other chemicals were obtained from the Aldrich Chemical Company. Nuclear magnetic resonance spectra were recorded at the frequencies reported with each spectra. Chemical shifts for protons are relative to $(CH_3)_4Si$ and fluorine relative to CCl_3F. Mass spectra were obtained on a Varian EM-600 or on a Finnegan GC/MS spectrometer. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer. Vapor-phase chromatography was accomplished with a Hewlett-Packard 5730-A flame ionization chromatograph. All XeF_2 reactions were carried out in standard glassware[13] in a well-ventilated hood since solid XeF_2 is toxic and has a vapor pressure of 4.6 mm at 25 °C.[14] The (difluoroiodo)benzene reactions were run in a 10-mL polyethylene bottle.

Reaction of XeF_2 with Butadiene (1). To a solution at −10 °C of butadiene (85 mg, 1.57 mmol) in the weighed amount of solvent to make 0.02 mole fraction butadiene was added 50.0 mg (0.295 mmol) of solid XeF_2. To the stirred mixture was added 0.2 equiv (with respect to XeF_2) of boron trifluoride etherate. The mixture was stirred for 10–15 min and then poured into an aqueous solution of 5% sodium bicarbonate, extracted with methylene chloride, and dried over anhydrous magnesium sulfate. Methylcyclohexane was added as an internal standard, and the products were analyzed (60–75% yields) by gas chromatography on a stainless steel column, 17 ft × $^1/_4$ in. 5% DNP on 80/100-mesh Chromosorb W. The product ratios are listed in Table I and are corrected for flame response. Analysis at 35 °C showed 3,4-difluoro-1-butene (**5**) and *trans*- and *cis*-1,4-difluoro-2-butene (**6t** and **6c**) to have retention times of 4.5, 10, and 11.5 min, respectively. Products **6c** and **6t** were collected by preparative VPC and found to have identical spectral properties as those synthesized independently (see below). Compound **5** could not be synthesized independently but was isolated by preparative VPC on the column above and gave the following spectral data: IR (CCl_4) 3010, 2960, 2830 (CH), 1670 (C=C), 1110 (CF), 980, 920, 890 (CH) cm^{-1}; ^{1}H NMR (270 MHz, C_6D_6) δ 4.05 (d, d, d, $J = 56.7$, $J = 26.0$, $J = 4.5$ Hz, 2 H), 4.72 (d, d, m, $J = 45.4$, $J = 17.3$ Hz, 1 H), 5.04 (d, d, $J = 10.3$, $J = 1.0$ Hz, 1 H), 5.19 (d, d, $J = 15.0$, J 1.0 Hz, 1 H), 5.53–5.65 (m, 1 H); mass spectrum, m/e (relative intensity) 92 (6).

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[12] Schmid, G. H.; Yeroushalmi, S.; Garratt, D. G. *J. Org. Chem.* **1980**, *45*, 910.

[13] A benchtop procedure for fluorination with XeF_2 has been reported; see ref 1b.

[14] "Halogen Chemistry"; Gurmann, V., Ed.; Academic Press: New York, 1967; Vol. 1, pp 409–411.

Synthesis of the Difluorides 6c and 6t. The reactions were done as reported in the literature.[8] The following data are presented here because the published synthesis does not indicate whether *cis*- or *trans*-1,4-dichloro-2-butene was used, nor were spectral data reported.[8] Thus, *trans*-1,4-difluoro-2-butene (**6t**) was prepared from *trans*-1,4-dichloro-2-butene in 64% yield, bp 75–76 °C, with the following spectral properties: IR (CCl_4) 3040 and 2950 (CH), 1680 (weak C=C), 1080 (CF), 980 (C=H) cm^{-1}; ^1H NMR 60 MHz (CCl_4) δ 4.93 (d, m, J = 45 Hz, 4 H), 5.60–6.30 (m, 2 H); ^{19}F NMR (254-MHz, neat) ϕ −159.1 (t, m, J = 45 Hz); mass spectrum, m/e (relative intensity) 92 (9). Similarly, *cis*-1,4-difluoro-2-butene (**6c**) was prepared from *cis*-1,4-dichloro-2-butene in 60% yield, bp 75–76 °C with the following spectral properties: IR (CCl_4) 3040, 2960, and 2890 (CH), 1660 (weak C=C), 1005 (CF), 890 (CH) cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 4.97 (d, m, J = 46 Hz, 4 H), 5.53–6.10 (m, 2 H); ^{19}F NMR (254 MHz, CCl_4) ϕ −159.2 (t, m, J = 46 Hz); mass spectrum, m/e (relative intensity) 92 (5).

Reaction of XeF_2 with 2,3-Dimethyl-1,3-butadiene (2). The reaction was done (25 mg of XeF_2) as described for **1** above with the following variations: temperature, 25 °C; 0.02 equiv of BF_3·ether; reaction time, 20 min. Analysis on a 17.5 ft × $^1/_8$ in. stainless steel column, 2.5% of FFAP on 80/100-mesh Chromosorb W at room temperature, showed >99% **7** and <1% **8** (80% yield) with retention times of 7 and 10 min, respectively. Compound **7** was collected by preparative VPC on a 14 ft × $^1/_4$ in. SS stainless steel column of 2.5% FFAP on 80/100-mesh Chromosorb W and gave the following spectral data: IR (CCl_4) 3010 and 2990 (CH), 1660 (C=C), 1040 (CF), 890 (CH) cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 1.47 (dd, J = 20.8, J = 2.2 Hz, 3 H), 1.87 (dd, J = 7.0, J = 1.0 Hz, 3 H), 4.33 (dd, J = 48.4, J = 18.4 Hz, 2 H), 5.10–5.30 (m, 2 H); mass spectrum, m/e (relative intensity) parent 120 (27), P − HF 100 (3.5), P − CH_2F 87 (100). Compound **8** was formed in less than 1% in methylene chloride but was formed in almost equal amounts in methanol as solvent. Attempted isolation of **8** formed in methanol was unsuccessful since it was too unstable. GC–mass spectral data for **8** at 20 eV gave prominent peaks at m/e (relative intensity) 99 (1), 70 (13), 61 (28), 45 (28), and 43 (100). Support for the existence of **8** was obtained by isomerization of **8** to **7**. A mixture of **7** and **8** (4:1) in methylene chloride with toluene as internal standard was found to rearrange to **7** at room temperature ca. 10 h.

Reaction of XeF_2 with *cis*- and *trans*-1,3-Pentadienes (3c and 3t). The reactions were as described for **2** above except boron trifluoride was not required as catalyst. Reactions proceeded smoothly at 0 °C for **3t** and **3c**. The reactions were complete in 10–15 min. Analysis by VPC (FFAP column above at room temperature gave **9t**, **10**, **11**, and **12** with retention times 4.3, 12, 14, and 17 min, respectively. Compound **9c**, retention time 5.4 min, was formed when the mixture was allowed to stand overnight at room temperature. The kinetic product distributions are given in Table II. Products **9c**, **9t**, and **12** were isolated by preparative VPC on the $^1/_4$ in. FFAP column above. The following spectral data were obtained. **9t**: ^1H NMR (360 MHz, $CDCl_3$) δ 1.72 (d, d, J = 6.4, J = 1.1 Hz, 3 H), 2.49 (t, m, J = 16.0 Hz, 2 H), 5.3–5.9 complex multiplets (However, when the methyl at δ 1.72 was decoupled the following data were obtained: δ 5.36 (d, t, J = 14.8, J = 6.2 Hz, 1 H), 5.63 (d, J = 14.8 Hz, 1 H), 5.68 (d, t, J = 14.8, J = 6.2 Hz, 1 H), 5.63 (d, J = 14.8 Hz, 1 H), 5.68 (t, t, J = 57, J = 4.7 Hz, 1 H). **9c**: ^1H NMR (360 MHz, $CDCl_3$) δ 1.67 (d, J = 7.0 Hz, 3 H), 2.58 (t, m, J = 16.0 Hz, 2 H), 5.35–5.43 (m, 2 H), 5.72 (t, t, J = 57, J = 4.7 Hz, 1 H). **12**: ^1H NMR (60 MHz, $CDCl_3$) δ 1.42 (d, d, J = 26.1, J = 7.1 Hz, 3 H), 5.05 (d, m, J = 50 Hz, 1 H), 6.00–6.40 (m, 2 H). Although **10** and **11** were stable to the mild reaction conditions, they rearranged to the 1,4-product **12** during isolation by preparative gas chromatography or when a mixture of the products remained overnight at room temperature in methylene chloride as solvent (toluene as internal standard).

Reaction of $C_6H_5IF_2$ with Dienes 1, 2, 3c, and 3t. (Difluoroiodo)benzene was prepared from (dichloroiodo)benzene in methylene chloride as described in the literature,[2] and its molarity (≈0.3 M) was determined by titration with thiosulfate. The $C_6H_5IF_2$ solution contains significant amounts of hydrogen fluoride which is required as catalyst. The hydrogen fluoride was removed by shaking the methylene chloride solution of $C_6H_5IF_2$ with anhydrous KF.[15] To 3.0 mL of the scrubbed $C_6H_5IF_2$ solution at 0 °C with stirring in a 10-mL polyethylene bottle was added a twofold excess of diene. Several drops of unscrubbed $C_6H_5IF_2$ solution were added to introduce hydrogen fluoride catalyst if the reaction did not proceed as indicated by titration with thiosulfate. The mixture was poured into an aqueous solution of sodium sulfite after 30 min at 0 °C. The organic layer was dried over anhydrous magnesium sulfate. Analysis by gas chromatography with the columns and internal standards used for the XeF_2 reactions above gave the kinetic distribution of products listed in Tables I and II. The yields were found to be 40–60% except for diene 1 which was found to be 20%.

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Registry No. **1**, 106-99-0; **2**, 513-81-5; **3c**, 1574-41-0; **3t**, 2004-70-8; **5**, 92901-60-5; **6c**, 92901-61-6; **6t**, 92901-62-7; **7**, 92901-63-8; **8**, 92901-64-9; **9c**, 92901-65-0; **9t**, 92901-66-1; **10**, 92901-67-2; **11**, 92901-68-3; **12**, 92901-69-4; XeF_2, 13709-36-9; $C_6H_5IF_2$, 26735-53-5.

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(15) Anhydrous KF is an efficient scrubber of hydrogen fluoride. The insoluable HKF_2 is formed.

Nucleophilic Substitution by Sulfite Ion on a Thiamin Analogue Having a Good Leaving Group

Georg Uray* and Ingo Kriessmann

Institut für Organische Chemie, Karl-Franzens-Universität,
A-8010 Graz, Austria

John A. Zoltewicz*

Department of Chemistry, University of Florida,
Gainesville, Florida 32611

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1′-Methylthiaminium ion[1,2] **1a** and its analogues having pyridine,[3,4] phenol,[3,5] or thiol[3,6] leaving groups (X in **1**) react with sulfite ion to give sulfonic acid betaine **2**. The mechanism of substitution is multistep,[2] Scheme I, rather than S_N2. The first step is the addition of the nucleophile to the pyrimidine ring to give intermediate **3** that expels the leaving group to produce resonance-stabilized cation **4**. Reaction of this cation with a second equivalent of nucleophile gives **5**, and this is followed by aromatization to yield the observed sulfonic acid substitution product **2**.

Because of the nature of the leaving groups employed to date it may be suggested that this complex mechanism is merely a consequence of the selection of departing groups ranked among those labeled "poor" and that an extra driving force may be necessary for their expulsion.

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