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## PRELIMINARY NOTE

## Carbanion Fluorination with Xenon Difluoride in the Presence of Sulfur (II) Derivatives

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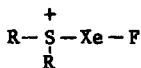
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## SUMMARY

An electrophilic fluorination reagent capable of fluorinating carbanions in moderate yield is obtained from the reaction of xenon difluoride with Sulfur II derivatives such as dimethyl sulfide.

Xenon difluoride,  $\text{XeF}_2$ , has displayed much utility and versatility in the fluorination of organic substrates[1a,b]. Among the various functional groups that react with this reagent, its reaction with sulfides is especially intriguing. Both Janzen[2] and Zupan[3] have observed the fluorination of sulfides with xenon difluoride to produce S,S-difluoro derivatives. Janzen noted the possibility of an intermediate fluorosulfonium ion, (A), in his work.

Moreover from the works of Bartlett[4], DesMarteau[5], and Gillespie[6] on compounds of xenon, one must also consider the involvement of an intermediate containing xenon, (B). We anticipated that either intermediate would exhibit greater stability when paired with a non-nucleophilic counter anion such as  $\text{BF}_4^-$  or  $\text{OTf}^-$  and would be capable of transferring fluorine to a carbanion. The results of our study are reported here.



The addition of one equivalent of  $\text{Me}_2\text{S}$  to a solution of  $\text{XeF}_2$  and  $\text{BF}_3\cdot\text{OEt}_2$  in dry  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$  under  $\text{N}_2$  produced a yellow semi-solid mixture. Heating to  $-20^\circ\text{C}$  was accompanied by a considerable evolution of gas, ( $\text{Xe ?}$ ), and resulted in a white-milky solution\*. To test the electrophilic nature of the intermediate, the sodium salts of the diethyl malonates were added to the initially formed yellow mixture. After usual work-up, (saturated  $\text{NaCl}$ - $\text{EtOAc}$  extraction), 42% diethyl fluoromalonates (1) were obtained. Table I shows the results of the fluorination of several alkylmalonates by this method\*\*

Table I	$\text{R}-\text{C}^-(\text{CO}_2\text{C}_2\text{H}_5)_2\text{Na}^+$	$\xrightarrow[\text{CH}_2\text{Cl}_2, -78^\circ\text{C}]{\text{XeF}_2, (\text{CH}_3)_2\text{S}, \text{BF}_3\cdot\text{OEt}_2}$	$\text{RFC}(\text{CO}_2\text{C}_2\text{H}_5)_2$ 1
	R	%Yield	$^{19}\text{F}$ Chemical Shift <sup>a</sup> /Multiplicity
	H	42	-118.7; d
	$\text{CH}_3$	32	-81.7; q
	$\text{C}_2\text{H}_5$	45	-92.93; t
	$\text{C}_5\text{H}_{11}$	30	-83.76; m
	$\text{PhCH}_2$	40	-88.44; t
	$\text{NO}_2$	0	none

<sup>a</sup> Chemical shifts upfield from TFA.

Mechanistically the reaction is particularly interesting. When  $\text{Me}_2\text{S}$  was used a low yield of -SMe derivative of the malonates, (2), was observed by  $^1\text{H}$  NMR spectroscopy. However, such side products were not observed when diphenyl or di-tert-butyl sulfides were used. Also, diethyl nitromalonate did not produce any fluorinated product, and only dimerized product, (3), was isolated quantitatively. In order to understand the effects of Lewis acids, the stoichiometric ratio of the reactants, and the reaction temperature several experiments were carried out. The results are summarized in Scheme I and Table II.

\* Elemental and Mass spectral analysis of the white solid showed the possible presence of trimethylsulfonium tetrafluoroborate.

\*\* Products were identified by  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectroscopy.

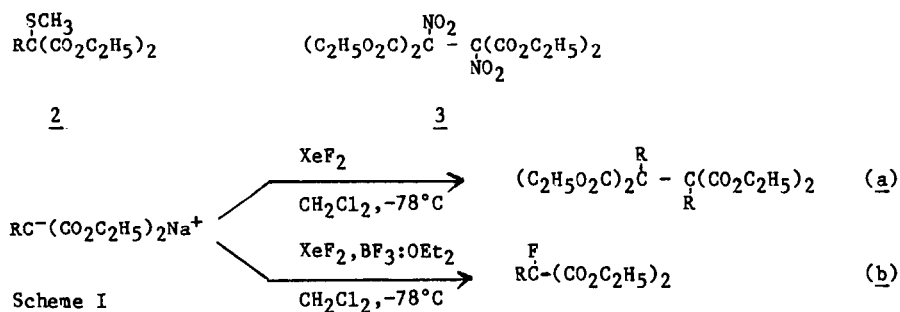
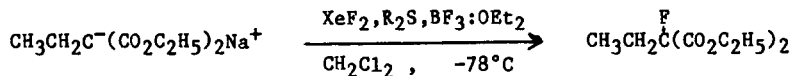


Table II



## Ratios

Malonate	BF <sub>3</sub> :OEt <sub>2</sub> or TMSOTf	XeF <sub>2</sub>	Sulfides	Temp.	%Yield*
1	1	1	1; Me <sub>2</sub> S	-78°C	45
1	1	2	1; Me <sub>2</sub> S	-78°C	20
1	1	2	1; Me <sub>2</sub> S	-20°C	5
1	1	1	1; t-Bu <sub>2</sub> S	-78°C	40
1	1	1	1; Ph <sub>2</sub> S	-78°C	35
1	3	3	3; Me <sub>2</sub> S	-78°C	30
1	1	1	1; Me <sub>2</sub> S	-100°C	40

\*based on <sup>19</sup>F NMR analysis

As Table II and Scheme I show, changing the stoichiometry of the reagents and substrates, the reaction temperature, or the sulfide structure can affect the yield of the reaction. However, an equal ratio of the reagents and malonates at low temperature ( -78°C) seems most favorable. The reaction of the malonates with XeF<sub>2</sub> in the absence of both the sulfides and BF<sub>3</sub>:OEt<sub>2</sub> or TMSOTf, produced only dimeric products, (reaction a, Scheme I), whereas in the presence of only BF<sub>3</sub>:OEt<sub>2</sub>, a low yield, 10%, of the fluorinated products was observed (reaction b).

The importance of  $\text{XeF}_2$  in this reaction became more obvious when elemental fluorine,  $\text{F}_2$ , was used as the fluorinating agent in place of  $\text{XeF}_2$  under identical conditions; no fluoromalonates were obtained. Furthermore, S,S-difluoro intermediates such as those detected and isolated by Zupan[3] and Janzen[2], are absent under our anhydrous reaction conditions as evidenced by the absence of appropriate known  $^{19}\text{F}$  NMR signals for the products, and the sulfides are detected or recovered unchanged.

Our preliminary low-temperature NMR studies show that when the  $^{19}\text{F}$  NMR spectrum of  $\text{XeF}_2$  was observed in  $\text{CDCl}_3$  solution at  $-55^\circ\text{C}$  its singlet and  $^{129}\text{Xe} - ^{19}\text{F}$  coupled satellites ( $J = 5665$  Hz) were observed at  $-97.1$  ppm upfield from trifluoroacetic acid to converge to a single line at  $-55$  ppm. On raising the temperature a transient Xe-F spectrum is observed again at  $0^\circ\text{C}$  at  $-96.5$  ppm (from TFA), with  $^{129}\text{Xe} - ^{19}\text{F}$  satellites ( $J = 5580$  Hz). The transient species is considered to be the sulfur xenon-fluoride, (B), which is consistent with the observed chemical and spectral properties\*. The alternate non-xenon containing intermediate, A, ( $\text{BF}_4^-$ ), is considered less likely because we have been unable to obtain a fluorination reagent by reacting dimethyl sulfide with elemental fluorine in the presence of  $\text{BF}_3 \cdot \text{OEt}_2$ [7].

In conclusion, the present study provides a new method for the in situ fluorination of carbanions [8]. Applications to other substrates and investigation into the structure of the intermediate are in progress.

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\* These spectral data are consistent with data reported for other XeF species. c.f. ref. 6.

Fluoride ion is determined not to be responsible for fluorination in this system as added Fluoride -18 was not incorporated in the final product.

- 1 a. M. Zupan, Xenon Halide Halogenation in S. Patai and Z. Rappaport (eds.) The Chemistry of Functional Groups. Supplement D., Wiley New York, 1983, p. 657; b. G.L. Cantrell and R. Filler, J. Fluorine Chem., 27 (1985) 35.
- 2 A.F. Janzen, P.M.C. Wang and A.E. Lemire, J. Fluorine Chem., 22 (1983) 557; R.K. Marat and A.F. Janzen, Can. J. Chem., 55 (1977) 3031.
- 3 M. Zupan, J. Fluorine Chem 8 (1976) 305; B. Zajc and M. Zupan J. Chem. Soc., Perkin I (1987) 965.
- 4 N. Bartlett, M. Weschberg, F.O. Sladky, P.A. Bulliner, G.R. Jones, and R.D. Burbank, Chem. Commun. (1969) 703; M. Weschberg, P.A. Bulliner, F.O. Sladky, R. News and N. Bartlett Inorg. Chem., 11 (1972) 3063.
- 5 J. Foropoulos, Jr. and D. Desmarteau J. Am. Chem. Soc., 104 (1982) 4260.
- 6 R.J. Gillespie, A. Netzer and G.H. Schrobilgen, Inorg. Chem., 13 (1974) 1455.
- 7 Olah and coworkers have obtained bromination and chlorination reagents from the reaction of dimethylsulfide with bromine or chlorine; G.A. Olah, L. Ohannesian and M. Arvanaghi, Synthesis (1986) 868.
- 8 S.T. Purrington, B.S. Kagen and T.B. Patrick, Chem. Rev., 86 (1986) 977; R.E. Banks and J.C. Tatlow in R.E. Banks, D.W.A. Sharp, J.C. Tatlow (eds.) Fluorine - The First Hundred Years, Elsevier Sequoia, Lausanne, 1986, p. 227.