anilide, 31819-75-7; 2-chlorophenazine-7-sulfonamide, 31819-76-8; 2,7-dichlorophenazine, 3372-79-0; trimethylammonium azobenzene-4,4′-disulfonate, 3819-78-0; pyridinium azobenzene-4,4′-disulfonate, 31819-79-1; azobenzene-4,4′-di(sulfonyl-*N*-dimethylamine), 31819-80-4; azobenzene-4,4′-di(sulfonyl-*N*-diethylamine), 31819-81-5; azobenzene-4,4′-disulfonanilide, 31819-82-6; azobenzene-4,4′-di(sulfonyl-*N*-methylaniline), 31819-83-7; barium 2-chlorobenzene-4,4′-disulfonate, 31819-84-8; 2-chloroazobenzene-4,4′-disulfonanilide, 31815-05-1; 4-chloroazobenzene-4′-sulfonyl-*N*-diethylamine, 31815-06-2; 4-chloroazobenzene-4′-sulfonyl-*N*-methylaniline, 31815-07-3; sodium phenazine-2,7-disulfonate, 31815-08-4; potassium phenazine-2,7-disulfonate, 31815-09-5; barium phenazine-2,7-disulfonate, 31815-10-8; triethylammonium phenazine-2,7-disulfonate, 31815-11-9; 2-chlorophenazine-7-sulfonanilide, 31815-12-0.

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Photodifluoramination of Fluoromethane

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Photodifluoramination of alkanes with N_2F_4 at 253.7 nm involves the steps[1] shown in eq 1–5. When methane is subjected to this reaction, HCN is produced by unimolecular elimination of HF from chemically activated CH_3NF_2,[2] a system that has been used as an elimination chemical laser.[3] We report now the photodifluoramination of fluoromethane, a case which contrasts dramatically with that of methane.

$$N_2F_4 \longrightarrow 2NF_2 \quad (1)$$

$$NF_2 \xrightarrow{h\nu} NF + F \quad (2)$$

$$R\text{-}H + F \longrightarrow HF + R \quad (3)$$

$$R + NF_2(N_2F_4) \longrightarrow R - NF_2 \quad (4)$$

$$NF + NF_2 \longrightarrow N_2F_2 + F \quad (5)$$

(1) C. L. Bumgardner, E. L. Lawton, K. M. McDaniel, and H. H. Carmichael, *J. Amer. Chem. Soc.*, **92**, 1311 (1970).

(2) C. L. Bumgardner, E. L. Lawton, and H. Carmichael, *Chem. Commun.*, 1079 (1968).

(3) T. D. Padrick and G. C. Pimentel, *J. Chem. Phys.*, **54**, 720 (1971).

Irradiation of an equimolar mixture of CH_3F and N_2F_4 in a Pyrex vessel for 30 min at a total initial pressure of 108 Torr gave the results summarized in eq 6.

$$\begin{array}{lll} & CH_3F + N_2F_4 \xrightarrow{253.7\ nm} & \\ \text{mmoles} & 2.18 \quad 2.23 & \\ & CH_3F + FCH_2NF_2 + (FCH_2)_2 + & \\ & 0.02 \quad 2.02 \quad 0.05 & \\ & N_2F_2 + SiF_4 + N_2O + N_2 & (6) \\ & 0.99 \quad 0.55 \quad 0.27 \quad 0.10 & \end{array}$$

The reaction was monitored by quantitative mass spectrometry. Products were separated by trap-to-trap distillation and the contents of each trap were examined by mass and infrared spectrometry and by gas chromatography.

During photodifluoramination of CH_4 under these reaction conditions, significant unimolecular elimination of HF occurs from CH_3NF_2 which is vibrationally excited. However, if the FCH_2NF_2 formed as described suffers any loss of HF at all, the amount of elimination must be several orders of magnitude lower than elimination from CH_3NF_2. Mass balances indicate that 94% of the carbon introduced as CH_3F is accounted for by FCH_2NF_2 and recovered CH_3F. We conclude therefore that $(k_2/k_1)_{FCH_2NF_2} \gg (k_2/k_1)_{CH_3NF_2}$.

$$CH_3 + NF_2(N_2F_4) \longrightarrow CH_3{}^*NF_2 \begin{cases} \xrightarrow[k_2]{M} CH_3NF_2 \\ \xrightarrow[k_1]{} HCN + 2HF \end{cases}$$

The remarkable effect produced by replacing one of the C–H bonds in the above system with a C–F bond may be due to the greater capacity of a C–F bond to store excess vibrational energy.[4,5] The presence of a C–F linkage also may increase the activation energy for HF elimination across the C–N bond of a difluoramine.[6]

Formation of FCH_2CH_2F is undoubtedly due to some coupling of the FCH_2 radical intermediates, the first time this process has been observed in the photodifluoramination reaction. The higher concentration of NF_2 and N_2F_4 relative to that of the alkyl radical (R) generated in step 3 generally makes step 4 much more important than dimerization of R.

Experimental Section[7]

Caution: Tetrafluorohydrazine and derivatives should be handled with care. Operations were conducted routinely behind shields.

Photodifluoramination of Fluoromethane.—In an apparatus described previously for the photodifluoramination of methane,[1] 2.18 mmol of fluoromethane (99.0%, Matheson) and 2.23 mmol

(4) J. T. Bryant, B. Kirtman, and G. O. Pritchard, *J. Phys. Chem.*, **71**, 3439 (1967); D. Sianesi, G. Nelli, and R. Fontanelli, *Chem. Ind. (Milan)*, **40**, 619 (1968).

(5) J. A. Kerr, D. C. Phillips, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1086 (1968).

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(7) Proton nuclear magnetic resonance, fluorine nuclear magnetic resonance, infrared, and mass spectra were obtained using the following instruments, respectively: Varian HA-100 high-resolution spectrometer, Varian DA 60 high-resolution spectrometer, Beckman IR-5A spectrophotometer, and Consolidated Model 620 and Associated Electronics Model MS902 mass spectrometers. Nmr spectra were run as approximately 5% by volume solutions in deuteriochloroform with the probe temperature at 25°. Fluorine (^{19}F) chemical shifts (ϕ) are in parts per million relative to fluorotrichloromethane as an external reference. Proton (^1H) chemical shifts (δ) are in parts per million downfield relative to tetramethylsilane as an internal reference.

of N_2F_4 (99.3%)[8] were irradiated for 30 min at a total initial pressure of 108 Torr. The reaction mixture was then distilled in a vacuum line equipped with stopcocks and joints lubricated with Kel-F90 fluorocarbon grease. Further purification was achieved by gas phase chromatography using a 10 ft × 0.375 in. copper column containing 30% by weight of QF-1 on 60–80 mesh Chromosorb P, helium as carrier gas, and a thermal conductivity cell as detector. 1,2-Difluoroethane, N_2F_2,[9] N_2O, N_2, and SiF_4 were identified by comparison of infrared and mass spectra with those of authentic samples. The ^{19}F nmr spectrum of $F^aCH_2NF_2{}^b$ showed a triplet at ϕ 202.8 (F^a) and a signal at ϕ −27.6 (F^b) in the ratio of 1:2, respectively. In the ^1H nmr spectrum absorption occurred at δ 5.15 (doublet in triplet). The coupling constants, $J_{F^aH} = 48$ and $J_{F^bH} = 22$ Hz, agree with data on similar compounds.[1] Bands (cm^{-1}) in the infrared spectrum of FCH_2NF_2 were observed at 2950 (CH), 1130, 1125 (CF), and at 940, 935, 929, 860, 845 (NF_2). The mass spectrum showed peaks at *m/e* corresponding to 85 (parent), 46 (FCHN), 33 (FCH_2), 28 (CH_2N), and 27 (CHN). The results shown in eq 6 were obtained by quantitative mass spectral analyses using pure samples for calibration. The reaction was repeated twice at a total initial pressure of 108 Torr and twice at 216 Torr with similar product yields.

Registry No.—Fluoromethane, 593-53-3; N_2F_4, 10036-47-2.

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(8) Kindly supplied by the Gorgas Laboratory, Rohm and Haas Co., Huntsville, Ala.

(9) Both *cis* and *trans* forms obtained: R. Ettinger, F. A. Johnson, and C. B. Colburn, *J. Chem. Phys.*, **34**, 2187 (1961); R. H. Sanborn, *ibid.*, **33**, 1855 (1969); S. King and J. Overend, *Spectrochim. Acta*, **22**, 689 (1966).

Side-Chain Amination during the Reaction of Methylbromothiophenes with Potassium Amide[1]

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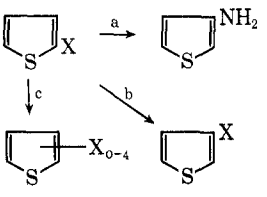
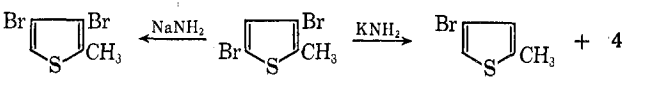
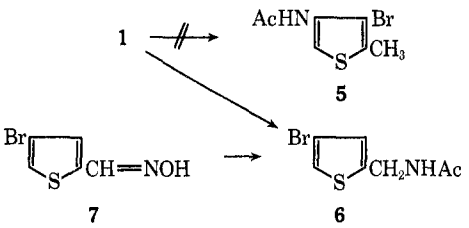
The reaction of α-bromo- and α-iodothiophenes with metal amides leads to cine amination (path a), halogen rearrangement (path b), and/or halogen disproportionation (path c) depending on the reaction conditions and the specific compounds involved.[2] This paper reports a fourth possible reaction of this system.



Although 2-methyl-3,5-dibromothiophene (**1**) reacts[3] with sodium amide according to path b (**1** → **2**), with potassium amide 2-methyl-4-bromothiophene (**3**) and an amine **4** (isolated as its acetamide **6**) are the only products obtained. Surprisingly, the spectral properties of this amide are inconsistent with those expected for a thienylacetamide such as **5** produced *via* path a and instead suggests the thenylacetamide structure **6**. This hypothesis was substantiated by the independent

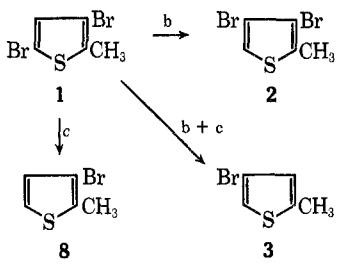




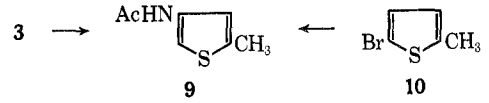
preparation of **6** from the oxime **7** of 4-bromothiophene-2-carboxaldehyde.[4]

The conversion of **1** to **4** probably involves paths b and c, side-chain bromination, and subsequent displacement of the resulting reactive[5] thenyl bromine by amide ion. In order to specify the sequence of the first three of these steps an attempt was made to intercept and/or test possible reaction intermediates.

At −60° the reaction of **1** with potassium amide gives as the major product **2** (path b) with minor amounts of **3** (paths b and c) and **8** (path c). Both **2** and **3** were treated with potassium amide at −33° followed by acetic anhydride to determine if any thenylamide **6** was formed. In the first case it was, while in the second



case it was not (85% recovery of **3**). The only amide found in this last reaction was the thienylacetamide **9**, formed by normal substitution. This same amide is the



only one obtained from the reaction of **10**[6] with potassium amide.[3]

(1) Abstracted in part from the Ph.D. dissertation of H. W. A., Texas Christian University, 1968.

(2) (a) M. G. Reinecke and H. W. Adickes, *J. Amer. Chem. Soc.*, **90**, 511 (1968); (b) M. G. Reinecke, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), C68 (1968).

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(5) S. Gronowitz, *Advan. Heterocycl. Chem.*, **1**, 88 (1963).

(6) The reported[7] preparation of **10** by the reaction of 2-methylthiophene with *N*-bromosuccinimide (NBS) has on occasion[3] proceeded well in our hands. On other occasions,[1] however, this procedure has led to extensive or even complete formation of 2-thenylbromide. This fickle nature of NBS is well known[8] and understood[9] but nevertheless difficult to control, at least in our hands. For this reason a reliable, alternative synthesis of **10** is described in the Experimental Section.

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