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 ^{1}H 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.

Acknowledgment.—We are grateful to the National Science Foundation for generous support of this work and to the National Aeronautics and Space Agency for a fellowship for E. L. L.

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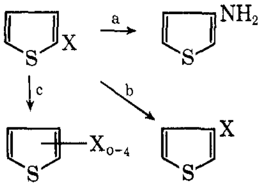
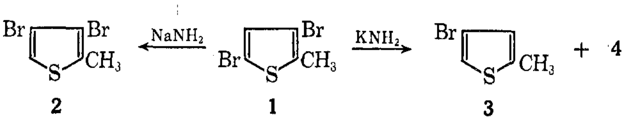
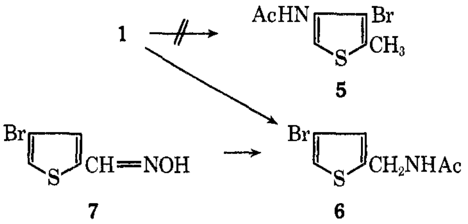
The reaction of α-bromo- and α-iodothiophenes with metal amides leads to cine amination (path a), halogen rearrangement (path b), and/or halogen disproportionation (path c) depending on the reaction conditions and the specific compounds involved.[2] This paper reports a fourth possible reaction of this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



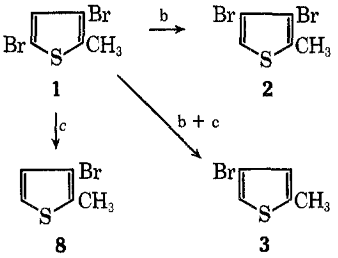
ties of this amide are inconsistent with those expected for a thienylacetamide such as 5 produced *via* path a and instead suggests the thenylacetamide structure 6. This hypothesis was substantiated by the independent

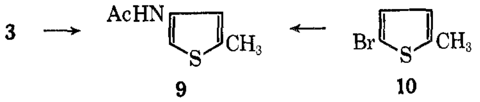


preparation of 6 from the oxime 7 of 4-bromothiophene-2-carboxaldehyde.[4]

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).

[3] M. G. Reinecke, H. W. Adickes, and C. Pyun, *J. Org. Chem.*, **36**, 2690 (1971).

[4] S. Gronowitz, P. Moses, A. Hornfeldt and R. Hakansson, *Ark. Kemi*, **17**, 165 (1961).

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

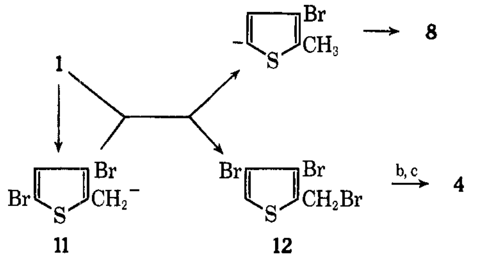
[6] The reported[7] preparation of **10** by the reaction of 2-methylthiophene with *N*-bromosuccinimide (NBS) has on occasion[3] proceeded well in our hands. On other occasions,[1] however, this procedure has led to extensive or even complete formation of 2-thenylbromide. This fickle nature of NBS is 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.

[7] K. D. Dittmer, R. P. Martin, W. Herz, and S. J. Cristol, *J. Amer. Chem. Soc.*, **71**, 1201 (1949).

[8] N. B. Chapman and J. F. A. Williams, *J. Chem. Soc.*, 5044 (1952).

[9] H. J. Dauben, Jr., and L. L. McCoy, *J. Amer. Chem. Soc.*, **81**, 4863 (1959).

These results suggest that side-chain bromination requires that more than one bromine atom be attached to the thiophene ring. A possible mechanism for this reaction which is consistent with this observation as well as our previous investigations[2] involves initial formation of a thenyl carbanion **11** in which the negative charge is partially stabilized by the cumulative inductive effects of the bromine atoms. This carbanion attacks a labile[10] α-bromine atom of a bromothiophene such as **1** to generate thenyl bromide **12** and the dehalogenated thiophene **8**.



Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were taken as films or KBr disks on a Beckman IR-10 or a Perkin-Elmer 237 instrument and were calibrated with a polystyrene film. Nmr spectra were obtained with a Varian A-60A instrument and calibrated with TMS as an internal reference. A Finnegan 1015SL quadrupole mass spectrometer was used for the mass spectrum determination. Gas chromatographic analysis was carried out on an Aerograph Autoprep A-700 using a 14 ft × 0.25 in. column of 20% DC QF-1 on Chromosorb W. Analyses were performed at M-H-W Laboratories, Garden City, Mich.

Reaction of 2-Methyl-3,5-dibromothiophene (1) with Potassium Amide.—Following the previously described procedure,[3] 5.2 g (0.02 mol) of **1** was treated with 0.12 mol of KNH_2 in 150 ml of liquid NH_3 for 15 min. After the usual work-up procedure,[3] the neutral fraction consisted of 0.5 g (14%) of 4-bromo-2-methylthiophene (**3**) identified by a comparison of its infrared spectrum with that of an authentic sample.[3] The basic fraction was acetylated and worked up as previously described[3] to give 0.71 g (15%) of the thenylacetamide **6**, mp 89–89.5°, whose infrared and nmr spectra were identical with those of a synthetic sample prepared as described below.

A vpc analysis of the neutral fraction from a similar reaction carried out at −60° showed the presence of starting material **1** (27%), 3,4-dibromo-2-methylthiophene (**2**) (24%), 4-bromo-2-methylthiophene (**3**) (5%), and 3-bromo-2-methylthiophene (**8**) (3%). Each of these products was identified by a comparison of its vpc retention time and spectral properties with those of authentic samples.[3]

4-Bromo-2-thiophenealdehyde Oxime (**7**).—The crude 4-bromo-2-thiophenealdehyde obtained from the reaction of 2.42 g (0.01 mol) of 2,4-dibromothiophene, 0.01 mol of BuLi in hexane, and 0.1 mol of DMF by the procedure of Gronowitz[4] was converted to 0.7 g (34%) of the oxime **7**: mp 150–151.5° (recrystallized from H_2O with the aid of Norit); ir 3200, 2870, 1645, 935, 900, 875, 830, 755 cm^{-1}.[11]

Anal. Calcd for C_5H_4BrNOS (**7**): C, 29.14; H, 1.96; N, 6.80. Found: C, 28.91; H, 1.90; N, 6.59.

2-Acetamidomethyl-4-bromothiophene (**6**).—A mixture of 0.21 g (0.001 mol) of **7**, 25 ml of ether, and 3 g (0.1 mol) of $LiAlH_4$ was heated under reflux for 2 hr. After destruction of the excess $LiAlH_4$ with wet ether the filtered solution was treated with 5 ml of acetic anhydride. Removal of the solvents on a rotary evaporator left a residue which was recrystallized from H_2O to give 0.11 g (47%) of **7**: mp 88.5–89°; nmr (CF_3COOH) τ 7.62 (s, 3, CH_3), 5.28 (d,[13] J = 5 Hz, 2, CH_2), 3.03 (m, 1, 5 H),[15] 2.86 (d, J = 1.8 Hz, 1, 3 H),[15] 1.50 (s, 1, NH); ir 3305, 1648, 1548, 825, 735 cm^{-1}.[11]

Anal. Calcd for C_7H_8BrNOS (**6**): C, 35.91; H, 3.44; N, 5.98. Found: C, 36.14; H, 3.60; N, 5.87.

Reaction of 3,4-Dibromo-2-methylthiophene (2) with Potassium Amide.—Following the previously described procedure,[3] 5.08 g (0.0197 mol) of **2** was treated with 0.039 mol of KNH_2 in liquid NH_3 at −33° for 15 min. The neutral fraction after work-up contained 2.8 g (55%) of recovered starting material, **2**, identified by its infrared spectrum. The acetylated basic fraction yielded 0.15 g (6%) of **6**, mp 88–89°, whose nmr and infrared spectrum were identical with those of authentic **6**.

Reaction of 4-Bromo-2-methylthiophene (3) with Potassium Amide.—One gram (0.00565 mol) of **3**[3] and 0.017 mol of KNH_2 were treated as above to give 0.85 g (85%) of recovered **3** in the neutral fraction. The acetylated basic fraction yielded a few milligrams of a white solid whose infrared spectrum was identical with that of **9** obtained as described below.

4-Acetamido-2-methylthiophene (**9**).—The acetylated basic fraction from the reaction of 2-bromo-5-methylthiophene (**10**) with potassium amide (reaction **1b** → **2b** in ref 3) contained a small amount (7%) of a tan, amorphous solid which after sublimation and crystallization from methanol–water gave white plates of **9**: mp 118–120°; nmr ($DCCl_3$) τ 7.90 (s, 3, CH_3CO), 7.60 (d, J = 1 Hz, 3, CH_3), 3.30 (m, 1, 5 H), 2.80 (d, J = 1 Hz, 1, 3 H); ir 3260, 1650, 820, 735 cm^{-1};[12] mass spectrum (70 eV) m/e (rel intensity) 155 (21), 113 (52), 112 (23), 80 (40), 45 (63), 43 (100), 39 (36), 28 (40), 15 (39).

Anal. Calcd for C_7H_9NOS (**9**): C, 54.16; H, 5.84; N, 9.03. Found: C, 54.38; H, 5.58; N, 8.82.

2-Bromo-5-methylthiophene (**10**).—To a solution of 7.3 g (0.075 mol) of 2-methylthiophene in 35 ml of dioxane was added 12 g (0.075 g-atom) of Br_2 in 75 ml of dioxane over a period of 1.5 hr. The reaction mixture was stirred at room temperature for an additional 5 hr and then treated with 400 ml of 10% $NaHCO_3$. The oily layer which separated was removed and the water layer was extracted with three 100-ml portions of ether. The combined oil and ether extracts were washed with two 50-ml portions of H_2O and dried (Na_2SO_4), and the ether was removed by distillation through a 40-cm Vigreux column. The residue was analyzed by vpc and the major product (84% yield) was identified as 2-bromo-5-methylthiophene (**10**), bp 68–69° (17 mm), by a comparison of its spectral properties with those of an authentic sample.[3,7]

Registry No.—**1**, 29421-73-6; **2**, 30319-01-8; **3**, 29421-92-9; **6**, 31767-00-7; **7**, 31767-01-8; **9**, 31767-02-9; **10**, 765-58-2; potassium amide, 17242-52-3.

Acknowledgment.—This research was generously supported by The Robert A. Welch Foundation and the Texas Christian University Research Foundation.

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(10) P. Moses and S. Gronowitz, *Ark. Kemi*, **18**, 119 (1961).

(11) Although the region from 806–826 cm^{-1} is usually cited[12] as being characteristic of 2,4-disubstituted thiophenes, many such compounds also appear to have strong absorptions from 720 to 760 cm^{-1}.[1,3,12]

(12) S. Gronowitz, P. Moses, and A. Hornfeldt, *Ark. Kemi*, **71**, 237 (1961).

(13) This apparent doublet is also found in the nmr of the acetamide of the benzylamine (4.17 τ, J = 6 Hz in CCl_4) and is probably due to restricted rotation around the amide bond.[14]

(14) L. A. LaPlanche and M. T. Rogers, *J. Amer. Chem. Soc.*, **85**, 3728 (1963).

(15) A. R. Katritzky, "Physical Methods in Heterocyclic Chemistry," Vol. II, Academic Press, New York, N. Y., 1963, pp 117–121.

Boron Photochemistry. VIII. Oxidative Photocyclization of Anilinoboranes

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In a recent publication[1] we presented a novel photochemical synthetic route to the B-phenyl derivatives of

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(1) P. J. Grisdale and J. L. R. Williams, *J. Org. Chem.*, **34**, 1675 (1969).