H, 8.82; Cl, 23.85. Found: C, 56.50; H, 8.71; Cl, 23.94. **9** (X = I): IR (CCl_4) 2980, 2920, 1725, 1370, 1110 cm^{-1}; NMR (CCl_4) δ 1.90 (s, 6 H), 1.47–2.00 (m, 2 H), 2.13 (s, 3 H), 2.43–2.83 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.0, 38.0 (2 C), 43.3 (2 C), 50.4, 207.1. **11** (X = Br): IR (CCl_4) 2970, 1750, 1250, 1160 cm^{-1}; NMR (CCl_4) δ 1.50–2.70 (m, 7 H), 3.43 (d, J = 5.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.0, 37.0, 38.4, 38.9, 43.7, 216.9; mass spectrum, m/e 175.983 27, 177.981 40 (calcd for C_6H_9OBr 175.983 67, 177.981 63). **11** (X = Cl): IR (CCl_4) 1755 cm^{-1}; NMR (CCl_4) δ 1.50–2.96 (m, 7 H), 3.68 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.9, 38.2, 39.0, 42.5, 48.0, 217.1. **12**: IR (CCl_4) 2950, 2240, 1430 cm^{-1}; NMR (CCl_4) δ 1.80–2.67 (m, 4 H), 3.27 (t, J = 6.0 Hz, 2 H). **13**: IR (CCl_4) 3600–2400 (v br), 1700, 1420, 1210 cm^{-1}; NMR (CCl_4) δ 1.97–2.67 (m, 4 H), 3.23 (t, J = 6.0 Hz, 2 H), 10.90 (s, 1 H).

5-(Phenylsulfenyl)-2-pentanone. Aluminum chloride (2.5 mL, 1.4 M solution of $AlCl_3$ in acetonitrile, 3.5 mmol) was added via syringe to a solution containing 0.195 g (2.31 mmol) of **1** and 10 mL of acetonitrile under nitrogen. Thiophenol (0.48 mL, 4.63 mmol) was added via syringe, and the solution was heated at 55 °C for 15 h, cooled to room temperature, poured into 10% $NaHCO_3$, and extracted with ether. The organic phase was washed with water and brine and dried over magnesium sulfate. Removal of solvent in vacuo gave 0.688 g of a yellow oil. Purification by TLC (silica gel, 1000 μm; CH_2Cl_2) gave pure 5-(phenylsulfenyl)-2-pentanone: 0.1169 g (28% yield);; IR (CCl_4) 3060, 2930, 1718, 1590, 745, 695 cm^{-1}; NMR (CCl_4) δ 1.40–2.07 (m, 2 H), 2.00 (s, 3 H), 2.43 (t, J = 6.5 Hz, 2 H), 2.83 (t, J = 7.0 Hz, 2 H), 6.78–7.20 (m, 5 H).

Acknowledgment. We are pleased to acknowledge the partial support of this investigation by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by Grant No. IN-97E from the American Cancer Society. We thank Dr. Catherine E. Costello, Associate Director of the Massachusetts Institute of Technology, Mass Spectrometry Laboratory (NIH Division of Research Resources Grant No. RR00317), for the high-resolution mass spectra.

Registry No. 1, 765-43-5; 2, 872-75-3; 3, 5771-58-4; 4, 4160-49-0; 5, 5500-21-0; 6, 1759-53-1; 7 (X = I), 3695-29-2; 7 (X = Br), 3884-71-7; 7 (X = Cl), 5891-21-4; 7 (X = SPh), 81358-55-6; 8 (X = I), 82080-21-5; 9 (X = I), 82080-22-6; 9 (X = Cl), 82080-23-7; 10, 72003-75-9; 11 (X = I), 71987-94-5; 11 (X = Br), 82080-24-8; 11 (X = Cl), 66980-41-4; 12, 6727-73-7; 13, 7425-27-6; Me_3SiCl, 75-77-4; NaI, 7681-82-5; NaBr, 7647-15-6; LiCl, 7447-41-8; Me_3SiSPh, 4551-15-9; PhSH, 108-98-5; $ZnCl_2$, 7646-85-7; Me_3SiI, 16029-98-4; NaCl, 7647-14-5; 4,4-dimethyl-2-pentanone, 590-50-1; 5-methyl-2-hexanone, 110-12-3.

General Route for the Facile Transformation of Ortho-Substituted Lithiobithienyls into Amino Derivatives

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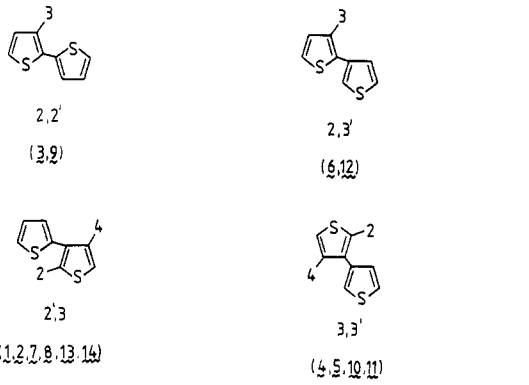
Received February 12, 1982

In the thiophene and bithienyl series, metalation and especially halogen–metal exchange with organolithium derivatives followed by the reaction of the thienyllithium derivatives with suitable electrophiles offers a most convenient route to many derivatives.[1,2] However, no convenient direct transformation of organolithium derivatives to amino derivatives is available. Recently, Trost[3] introduced azidomethyl phenyl sulfide as a synthon for NH_2^+. The reaction of Grignard reagents prepared directly or by the reaction of organolithium derivatives with magnesium bromide gave triazenes with azidomethyl phenyl sulfide which upon hydrolysis with strong alkali gave the amino derivatives in good yield. However, according to Trost this route fails with heteroaromatic organometallic reagents.

Chart I



We have for some time been interested in developing mild methods for the preparation of ortho-substituted aminobithienyls in connection with our interest in boron-containing aromatic heterocycles such as borazarobenzodithiophenes.[4] Also other interesting tricyclic systems could be prepared from ortho-substituted aminobithienyls, which like simple aminothiophenes are expected to be rather unstable. 2-Amino-3,3'-bithienyl has previously been obtained as the stannic chloride double salt by reduction of the nitro derivative, and the free amine was considered too unstable to be isolated.[5,6]

In a previous paper we reported a convenient method for the synthesis of azidothiophenes by reaction of the corresponding thienyllithium derivative with *p*-toluenesulfonyl azide followed by fragmentation of the resulting triazene salts.[7] As azidothiophenes can be reduced almost quantitatively to aminothiophenes by hydrogen sulfide[8] or lithium aluminum hydride, we investigated this two-step procedure to ortho-substituted aminobithienyls. The ortho-substituted azido derivatives themselves are interesting intermediates for the synthesis of hitherto unknown dithienopyrroles, which should be available by thermal decomposition.

Of the six possible ortho-substituted bromobithienyls, four have already been described in the literature, and the two hitherto unknown ones, viz., 4'-bromo-2,3'-bithienyl (**1**) and 2'-bromo-2,3'-bithienyl (**2**), were prepared by coupling reactions of (2-thienyl)copper with 3-bromo-4-iodothiophene and 2-bromo-3-iodothiophene, respectively.[9]

(2-Thienyl)copper reacts with 3-bromo-4-iodothiophene, prepared from 3,4-dibromothiophene by halogen–metal exchange and reaction with iodine, in pyridine–TMEDA

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Table I. Yields and Physical and IR and Mass Spectral Data[a] of Azidothiophenes 3-8

compd	yield, %	mp or bp (mm), °C	IR (N_3), cm^{-1}	MS, m/e
3-azido-2,2'-bithienyl (3)	72	110-112	2090	207 (M^+), 179
2-azido-3,3'-bithienyl (4)	41	*b*	2100	207 (M^+), 178
4-azido-3,3'-bithienyl (5)	77	56-57	2100	207 (M^+), 179
3-azido-2,3'-bithienyl (6)	73	92-95 (0.5)	2095	207 (M^+), 179
4-azido-2',3-bithienyl (7)	75	118-120 (0.5)	2110	207 (M^+), 179
2-azido-2',3-bithienyl (8)	33	*b*	2090	207 (M^+), 178

[a] Satisfactory elemental analyses were obtained for compounds 3 and 5-7. [b] These were obtained at low temperature as a light yellow solid (4) and a yellow oil (8) whose physical and analytical data could not be determined due to their decomposition at room temperature.

Table II. Yields and Physical and IR and Mass Spectral Data[a] of Aminothiophenes 9-14

compd	yield, %	mp or bp (mm), °C	IR (NH_2), cm^{-1}	MS, m/e
3-amino-2,2'-bithienyl (9)	92	150-152 (0.5)	3430-3360	181 (M^+), 136
2-amino-3,3'-bithienyl (10)	87	120-122 (0.5)	3430-3350	181 (M^+), 153, 136
4-amino-3,3'-bithienyl (11)	91	36-38	3440-3360	181 (M^+), 136
3-amino-2,3'-bithienyl (12)	93	108-110 (0.5)	3440-3360	181 (M^+), 136
4-amino-2',3-bithienyl (13)	95	97-98 (0.01)	3450-3360	181 (M^+), 136
2-amino-2',3-bithienyl (14)	71	*b*	3430-3350	181 (M^+), 153, 136

[a] Satisfactory elemental analyses were obtained for compounds 9-13. [b] This was obtained as yellow oil, unstable at room temperature, whose physical and analytical data were determined from the acetylamino derivative.

solution to give 1 (Chart I) in 55% yield based on the aryl iodide. (2-Thienyl)copper also reacted faster with the β-positioned iodine than the α-positioned bromine of 2-bromo-3-iodothiophene to give 2 in 53% yield.

The structures of 1 and 2 followed from their ^1H NMR[10] and mass spectra.

By halogen–metal exchange at low temperature the ortho-substituted bromobithienyls were converted to the corresponding lithium derivatives. Treatment of these derivatives with *p*-toluenesulfonyl azide and subsequent fragmentation of the intermediate triazene–lithium salts gave the azides 3–8. The 3-azido derivatives (3, 5–7), obtained in good yields, are stable compounds, but 2-azido-3,3'-bithienyl (4) and 2-azido-2',3-bithienyl (8), obtained in 30–40% yields, are somewhat unstable at room temperature but can be stored at −20 °C for extended periods. The instability observed with 2-azido compounds and the nature of the decomposition products are under investigation.[11] All ortho-substituted azidobithienyls were characterized by spectra and the 3-azido compounds by elemental analysis as well. Yields and physical and IR data are collected in Table I. IR spectra of all azido compounds showed the expected N_3 asymmetric stretching absorption in the region 2090–2110 cm^{-1}.

The structures of the azides 3–8 were confirmed by proton NMR spectra, which in all cases showed two superimposed systems due to the two and the three nuclei interacting in the di- and monosubstituted rings. The thiophene ring carrying an azido group gives rise to a characteristic AB system, with coupling constants in the range $J_{4,5}$ = 5.4–5.7 Hz for 3, 4, 6, and 8, and $J_{2,5}$ = 3.4 Hz for 5 and 7. The chemical shifts between the hydrogens in the azido-substituted groups are small, and certain assignment is difficult. However, on the basis of the electron-donating properties of the azido group,[12] the high-field doublets in 5 and 7 are assigned to the ortho hydrogens in the 5-positions. On similar grounds, but less certain, is the assignment of the high-field doublets to hydrogen 4 in 3 and 6 and to hydrogen 5 in 4 and 8. The monosubstituted thiophene ring of 3 and 5 gave very strongly coupled spectra, while the ABX spectra of 4 and 6–8 allow complete assignments to be carried out.

Of the various methods available for the reduction of azides to amines, we found treatment with hydrogen sulfide or with lithium aluminum hydride to be superior ones for the transformation of azides 3–8 into ortho-substituted aminobithienyls 9–14 (Table II).[13] The conversion was effected in nearly quantitative yields for the azides 3–7. No sign of decomposition was found for the amines 9–13, which are inert compounds and can be stored indefinitely in the refrigerator. Compound 14 (conversion yield 71%) is slightly labile but can be stored for a long time at −20 °C.

The structures of the less stable amines 10 and 14 were also confirmed by preparing their acetylamino derivatives, 15 and 16, respectively, which are stable, solid compounds. Yield and physical and spectral (IR, MS, NMR) data of the 2-(acetylamino)-3,3'-bithienyl (15) were identical with those reported in the literature. Yield and physical and analytical data of hitherto unknown 2-(acetylamino)-2',3-bithienyl (16) are reported in the Experimental Section.

IR spectra showed two expected peaks in the region 3360–3430 cm^{-1} for all amino compounds. In no case could the proton NMR spectra of these amines be interpreted as being due to the imino form. The spectra showed two adjacent systems due to the two and three interacting nuclei, characterized by $J_{4,5}$ = 5.3–5.7 Hz for 9, 10, 12, and 14 and by $J_{2,5}$ = 3.35 Hz for 11 and 13 for the AB part.

Due to the strong electron-donating effect of the amino group, assignment of the doublets in all compounds (9–14) is straightforward in the disubstituted thiophene part (cf. ref 10a). Only in the monosubstituted part of 12–14 were the chemical shift differences large enough to allow assignments.

We thus conclude from our results that the route ArLi → ArN_3 → $ArNH_2$ is a very satisfactory alternative to the

(10) For proton NMR spectra of several monosubstituted and disubstituted thiophenes, see: (a) Hoffman, R. A.; Gronowitz, S. *Ark. Kemi* **1960**, *16*, 515, 539. (b) Kellogg, R. M.; Wynberg, H. *J. Am. Chem. Soc.* **1967**, *89*, 3495.

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direct amination of ArM and is superior for heterocycles.

Experimental Section

Materials. 3,4-Dibromothiophene,[14] 2,3-dibromothiophene,[15] 2-bromo-3-iodothiophene,[16] 4-bromo-3,3′-bithienyl,[17] 2-bromo-3,3′-bithienyl,[17] 3-bromo-2,3′-bithienyl,[17] 3-bromo-2,2′-bithienyl[18] and *p*-toluenesulfonyl azide[19] were prepared as described in the literature.

Copper(I) bromide, from BDH, finely powdered, was stored at 110 °C. *n*-Butyllithium is a commercial product (Metallgesellschaft AG, 1.6 N in *n*-hexane). Diethyl ether, pyridine, and TMEDA were dried and stored under nitrogen.

Spectra. Infrared spectra, recorded with a Perkin-Elmer Model 257 instrument, are for solutions in carbon disulfide. ^1H NMR spectra were recorded on a JEOL NH-MH 100 in deuteriochloroform unless otherwise stated using Me_4Si as internal standard. Mass spectra were recorded on a Finnigan Model 4021 instrument.

GLC Analysis. GLC analyses were performed with a Varian Model 3700 instrument with a FID detector and with a ss column 50 cm × $^1/_8$ in. filled with 5% OV 101 on Chromosorb G-HP.

Preparation of 3-Bromo-4-iodothiophene. To a dry ethereal solution of 24.2 g (0.1 mol) of 3,4-dibromothiophene, cooled to −70 °C, was added 66 mL (0.1 mol) of *n*-butyllithium in *n*-hexane under nitrogen. After being stirred for 40 min at −60 °C, the reaction mixture was transferred with nitrogen into a dry ethereal solution of iodine (25.4 g, 0.1 mol). The reaction mixture was stirred for 5 h and, when the temperature reached −10 °C, hydrolyzed with water. After extraction with ether the combined organic layers were washed with water and dried over Na_2SO_4. The elimination of the solvent left a red oil which was chromatographed on aluminum oxide (Fluka Type 5016 A) column with petroleum ether (bp 30–60 °C) as an eluant. Finally, the colorless oil was distilled: bp 66–68 °C (0.5 mm); 22 g (76% yield); NMR δ 6.95 (2, q, J = 3.4 Hz); mass spectrum, m/e 290, 288. Anal. Calcd for C_4H_2BrIS: C, 16.62; H, 0.69; S, 11.09. Found: C, 16.60; H, 0.65; S, 11.00.

General Procedure for the Preparation of Ortho-Substituted Bromobithienyls 1 and 2. To a dry pyridine solution (80 mL) of (2-thienyl)copper, prepared according to ref 6a from thiophene (0.12 mol), *n*-butyllithium (0.1 mol), and copper(I) bromide (14.3 g, 0.1 mol), was added a solution of the appropriate iodothiophenes (30.0 g, 0.1 mol) in 10 mL of dry TMEDA. The mixture was refluxed, and the progress of the reaction was followed by GLC (flow rate of carrier 30 mL/min; temperature = 50–200 °C at 10 °C/min). When the ratio of iodoarenes/monobromobithienyls was constant (ca. 3–4 h), the mixture was cooled, and 200 mL of cold water was added. The solid halogen–copper compound was filtered off, and the solution was extracted three times with ether. The combined extracts were washed twice with cold 0.5 N HCl to remove the pyridine, with 10% Na_2CO_3 solution, and with water and dried over Na_2SO_4.

The crude reaction product was chromatographed on silica gel column with petroleum ether (bp 30–60 °C) as an eluant.

Unreacted iodothiophene derivatives were recovered first (ca. 3.0 g). A second fraction consisting mainly of ortho-substituted monobromobithienyls was distilled under vacuum.

4-Bromo-2′,3-bithienyl (1) was obtained as a colorless oil: 55% yield; bp 98–100 °C (0.5 mm); NMR δ 7.50 (q, 1, H-3′), 7.20 (s, 2, H-2, H-5), 7.18 (q, 1, H-5′), 6.97 (q, 1, H-4′); J(4′,5′) = 5.1 Hz, J(3′,4′) = 3.5 Hz, J(3′,5′) = 1.2 Hz; mass spectrum, m/e 246 and 244 (M^+), 165. Anal. Calcd for $C_8H_5BrS_2$: C, 39.19; H, 2.05; S, 26.15. Found: C, 39.22; H, 2.00; S, 26.02.

2-Bromo-2′,3-bithienyl (2) was obtained as a colorless oil: 53% yield; bp 110–112 °C (0.5 mm); NMR δ 7.38 (9, 1, H-3′), 7.20 (q, 1, H-5′), 7.05 (q, 2, H-4, H-5), 6.98 (q, 1, H-4′); J(4,5) = 5.70 Hz, J(4′,5′) = 5.0 Hz, J(3′,4′) = 3.5 Hz, J(3′,5′) = 1.1 Hz; mass spectrum, m/e 246 and 244 (M^+), 165. Anal. Calcd for $C_8H_5BrS_2$: C, 39.19; H, 2.05; S, 26.15. Found; C, 39.22; H, 2.01; S, 26.10.

General Procedure for the Preparation of Ortho-Substituted Azidobithienyls 3–8. A solution of the appropriate ortho-substituted bromobithienyls (12.2 g, 0.05 mol) in 50 mL of dry ether was added dropwise with stirring at −70 °C to *n*-butyllithium (32 mL, 1.6 N in *n*-hexane). The reaction mixture was stirred for 45 min at −70 °C, after which an ethereal solution of *p*-toluenesulfonyl azide (10 g, 0.055 mol) was added dropwise. After the addition was complete, the resulting mixture was stirred for 5 h at −70 °C. When the temperature had reached −10 °C, the resulting triazene salt was rapidly filtered off and washed with dry ether. The solid material was then suspended in 150 mL of ether and treated with a solution of 13.3 g (0.05 mol) of tetrasodium pyrophosphate in 200 mL of water. After the mixture was stirred overnight at 5 °C, the organic layer was separated, and the aqueous solution was extracted twice with ether.

The combined organic layers were washed with water and dried. The solvent was evaporated and the residue chromatographed on a Florisil column with *n*-pentane as an eluant.

2-Azido-3,3′-bithienyl (4) and 2-azido-2′,3-bithienyl (8) were prepared by the same procedure except that the fragmentation with sodium pyrophosphate was carried out with a precooled suspension (at −70 °C) of the triazene salt in *n*-pentane.

During the addition of the aqueous solution the temperature of the mixture increased. When it had reached 0 °C, the mixture was stirred for a few minutes and then iced at −20 °C. After one night at this temperature the upper organic phase was collected and dried, and the solvent was removed under vacuum at low temperature.

Almost pure azides 4 (as yellow solid) and 8 (as yellow oil) were recovered and stored at −20 °C. Yields and physical and IR data are collected in Table I.

3-Azido-2,2′-bithienyl (3): NMR δ 7.34–7.22 (m, 2, H-3′, H-5′), 7.15 (d, 1, H-5), 7.07–6.96 (q, 1, H-4′), 6.91 (d, 1, H-4); J(4,5) = 5.2 Hz; mass spectrum, m/e 207 (M^+), 179, 127. Anal. Calcd for $C_8H_5N_3S_2$: C, 46.35; H, 2.43; N, 20.27; S, 30.94. Found: C, 46.30; H, 2.41; N, 20.12; S, 30.80.

2-Azido-3,3′-bithienyl (4): NMR δ 7.52 (q, 1, H-2′), 7.44–7.26 (m, 2, H-4′, H-5′), 7.02 (d, 1, H-4), 6,88 (d, 1, H-5); J(4,5) = 5.7 Hz; mass spectrum, m/e 207 (M^+), 178, 166.

4-Azido-3,3′-bithienyl (5): NMR δ 7.47 (t, 1, H-2′), 7.29 (d, 1, H-2), 7.18 (d, 2, H-4′, H-5′), 6.91 (d, 1, H-5); J(2,5) = 3.3 Hz; mass spectrum, m/e 207 (M^+), 179, 108. Anal. Calcd for $C_8H_5N_3S_2$: C, 46.35; H, 2.43; N, 20.27; S, 30.94. Found: C, 46.38; H, 2.45; N, 20.33; S, 30.82.

3-Azido-2,3′-bithienyl (6): NMR δ 7.55 (q, 1, H-2′), 7.37–7.19 (m, 2, H-4′, H-5′), 7.09 (d, 1, H-5), 6.88 (d, 1, H-4); J(4,5) = 5.4 Hz; mass spectrum, m/e 207 (M^+), 179, 127. Anal. Calcd for $C_8H_5N_3S_2$: C, 46.35; H, 2.43; N, 20.27; S, 30.94. Found: C, 46.34; H, 2.47; N, 20.30; S, 30.91.

4-Azido-2′,3-bithienyl (7): NMR δ 7.34–7.27 (q, 1, H-3′), 7.22 (d, 1, H-2), 7.19–7.11 (q, 1, H-5′), 7.01–6.90 (q, 1, H-4′), 6.76 (d, 1, H-5); J(2,5) = 3.4 Hz; mass spectrum, m/e 207 (M^+), 179, 108. Anal. Calcd for $C_8H_5N_3S_2$: C, 46.35; H, 2.43; N, 20.27; S, 30.94. Found: C, 46.32; H, 2.41; N, 20.28; S, 30.88.

2-Azido-2′,3-bithienyl (8): NMR δ 7.40–7.18 (m, 2, H-3′, H-5′), 7.12–7.01 (q, 1, H-4′), 7.19 (d, 1, H-4), 6.94 (d, 1, H-5); J(4,5) = 5.6 Hz; mass spectrum, m/e 207 (M^+), 178, 166.

General Procedure for the Transformation of Azides 3–8 into Amino Derivatives 9–14. Reduction with Hydrogen Sulfide. The reductions of the azides 3–8 were carried out under the general conditions for hydrogen sulfide reduction described in ref 8. In each case, hydrogen sulfide was bubbled at 0 °C through a methanolic solution (20 mL) of azides (5 mmol) containing a few drops of piperidine. After 40 min the solution was allowed to warm to 20 °C, and the stream of hydrogen sulfide was continued at this temperature until TLC showed the absence of the starting material. The mixture was cooled to 0 °C and the precipitated sulfur was filtered off. The solvent was eliminated under vacuum and the residue chromatographed on an aluminum oxide column (Fluka Type 5016 A) with *n*-hexane as an eluant.

2-Amino-3,3′-bithienyl (10) and 2-amino-2′,3-bithienyl (14) were prepared by the same procedure except that the hydrogen sulfide was bubbled through the methanolic solution at −30 °C

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for 4 h. The solvent was removed under vacuum at low temperature, and the oily residue, consisting of a mixture of sulfur and amino derivatives, was purified through a Florisil column with *n*-pentane as an eluant.

After a first fraction, consisting of sulfur, 10% of diethyl ether in *n*-pentane was used as an eluant. The collected oil was composed of almost pure amino derivatives, and for compound **10** a distillation under vacuum was possible.

The acetylamino derivatives were prepared in a well-stirred diethyl ether mixture of acetyl chloride (1 equiv) and solid K_2CO_3 (1.5 equiv). After 4 h (TLC showed the absence of starting material), and the reaction mixture afforded a solid compound, which was crystallized from ligroin (bp 80–100 °C).

2-(Acetylamino)-3,3′-bithienyl (15) was obtained in 85% yield as a white solid, mp 113–115 °C (lit.[4] mp 110–115 °C).

2-(Acetylamino)-2′,3-bithienyl (16) was obtained in 83% yield as a white solid: mp 104–106 °C; NMR δ 8.04 (br s, 1, NH), 7.37–7.07 (m, 3, H-3′, H-4′, H-3′), 6.97 (d, 1, H-4 or H-5), 6.89 (d, 1, H-5 or H-4), 2.19 (s, 3, CH_3); $J(4,5)$ = 5.7 Hz; IR 3400 (NH), 1700 (>CO) cm^{-1}; mass spectrum, *m/e* 223 (M^+), 181. Anal. Calcd for $C_{10}H_9NOS_2$: C, 53.8; H, 4.06; S, 28.7. Found: C, 53.2; H, 4.24; S, 27.9.

General Procedure for the Transformation of Azides 3–8 into Amino Derivatives 9–14. Reduction with Lithium Aluminum Hydride. A suspension of hydride (1 g, 25 mmol) in dry ether (30 mL) was cooled to 0 °C, and the azidobithienyl (1 g, 5 mmol) in dry ether (20 mL) was added dropwise, maintaining the same temperature. The solution was stirred for 2 h after which it was allowed to warm to room temperature and was stirred at this temperature for 4 h (until TLC showed that no starting material was left). The mixture was cooled, and wet ether was added to destroy the excess of lithium aluminum hydride followed by cold distilled water to break up the complex. The resulting white solid was filtered off, and the filtrate was extracted with ether. The combined extracts were washed with water and dried, and the solvent was removed under vacuum. The oily residue was distilled under vacuum.

Yields and physical and IR data are collected in Table II.

2-Amino-3,3′-bithienyl (10) was prepared by the same procedure except that the suspension of hydride was cooled to 0 °C during the addition of a cooled (−20 °C) ethereal solution of azides. The reaction mixture was kept at this temperature for 2 h. The mixture was then allowed to warm slowly to room temperature and was stirred for an additional 2 h.

An attempt to reduce the 2-azido-2′,3-bithienyl (**8**) by the same procedure gave the corresponding amino compounds in low yield (32%).

3-Amino-2,2′-bithienyl (9): NMR δ 7.19 (m, 1, H-5′), 7.11–6.97 (m, 2, H-3′, H-4′), 7.00 (d, 1, H-5), 6.57 (d, 1, H-4), 3.79 (br s, 2, NH_2); $J(4,5)$ = 5.3 Hz; mass spectrum, *m/e* 181 (M^+), 136. Anal. Calcd for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.72; S, 35.38. Found: C, 52.93; H, 3.86; N, 7.64; S, 35.28.

2-Amino-3,3′-bithienyl (10): NMR δ 7.37–7.19 (m, 3, H-2′, H-4′, H-5′), 6.82 (d, 1, H-4), 6.47 (d, 1, H-5), 3.88 (br s, 2, NH_2); $J(4,5)$ = 5.4 Hz; mass spectrum, *m/e* 181 (M^+), 153, 136. Anal. Calcd for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.72; S, 35.38. Found: C, 52.98; H, 3.86; N, 7.69; S, 35.16.

4-Amino-3,3′-bithienyl (11): NMR δ 7.40–7.18 (m, 3, H-2′, H-4′, H-5′), 7.09 (d, 1, H-5), 6.19 (d, 1, H-2), 3.80 (br s, 2, NH_2); $J(2,5)$ = 3.6 Hz; mass spectrum, *m/e* 181 (M^+), 136. Anal. Calcd for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.72; S, 35.38. Found: C, 53.22; H, 3.95; N, 7.58; S, 35.12.

3-Amino-2,3′-bithienyl (12): NMR δ 7.40–7.20 (m, 3, H-2′, H-4′, H-5′), 7.01 (d, 1, H-5), 6.59 (d, 1, H-4), 3.53 (br s, 2, NH_2); $J(4,5)$ = 5.3 Hz; mass spectrum, *m/e* 181 (M^+), 136. Anal. Calcd for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.72; S, 35.38. Found: C, 52.91; H, 3.88; N, 7.69; S, 35.20.

4-Amino-2′,3-bithienyl (13): NMR δ 7.30–6.97 (m, 3, H-2′, H-4′, H-5′), 7.15 (d, 1, H-5), 6.19 (d, 1, H-2), 3.65 (br s, 2, NH_2); $J(4',5')$ = 5.0 Hz, $J(3',4')$ = 3.6 Hz, $J(3',5')$ = 1.2 Hz, $J(2,5)$ = 3.3 Hz; mass spectrum, *m/e* 181 (M^+), 136. Anal. Calcd for $C_8H_7NS_2$: C, 53.00; H, 3.89; N, 7.72; S, 35.38. Found: C, 52.90; H, 3.85; N, 7.74; S, 35.16.

2-Amino-2′,3-bithienyl (14): NMR δ 7.27–6.90 (m, 3, H-2′, H-4′, H-5′), 6.85 (d, 1, H-4), 6.49 (d, 1, H-5), 3.90 (br s, 2, NH_2). $J(4,5)$ = 5.6 Hz; mass spectrum, *m/e* 181 (M^+) 153, 136.

Acknowledgment. We thank Mrs. Ann Nordlund, Mrs. Kerstin Pettersson, and Mr. Einar Nilsson for technical assistance. Grants from the Swedish Natural Science Research Council to S.G. are gratefully acknowledged. P.Z. is grateful to CNR of Rome for a scholarship (No. 203.3.13), which made his stay in Lund possible.

Registry No. **1**, 82080-26-0; **2**, 82080-27-1; **3**, 82080-28-2; **4**, 82080-29-3; **5**, 82080-30-6; **6**, 82080-31-7; **7**, 82080-32-8; **8**, 82080-33-9; **9**, 82080-34-0; **10**, 74890-92-9; **11**, 82080-35-1; **12**, 82080-36-2; **13**, 82080-37-3; **14**, 60703-79-9; **15**, 74878-36-7; **16**, 82080-38-4; 3-bromo-4-iodothiophene, 73882-41-4; 3,4-dibromothiophene, 3141-26-2; (2-thienyl)copper, 5590-45-4; 2-bromo-3-iodothiophene, 24287-92-1; 4-bromo-3,3′-bithienyl, 28686-96-6; 2-bromo-3,3′-bithienyl, 82080-39-5; 3-bromo-2,3′-bithienyl, 28686-98-8; 3-bromo-2,2′-bithienyl, 19690-69-8; *p*-toluenesulfonyl azide, 941-55-9.

Behavior of *N*-*p*-Anisyl-*N*-*tert*-butylnitroxide in Nonaqueous Protic Acids

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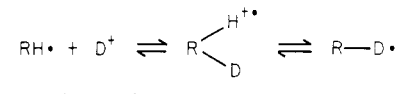
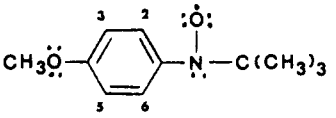
Received January 18, 1982

Recently, we[1] and others[2,3] have demonstrated that aryl carbocations will undergo an electrophilic substitution reaction with protons or deuterons in a nonaqueous acid medium. It occurred to us that aryl radicals should undergo a similar exchange reaction even more easily in these media. Clearly there are criteria which must be fulfilled before these reactions can be easily studied, especially by electron spin resonance (ESR) spectroscopy. First of all, the radical should be either long-lived (persistent) or, preferably, have an infinite lifetime. Secondly, the radical should be completely monomeric. If the radical were in equilibrium with a diamagnetic dimer, it would be difficult to tell which species is undergoing the substitution reaction. Finally, as many of the acids which are likely to be used in such a study are excellent oxidizing agents and many free radicals are easily oxidized, one must carefully match the radical with the acid.



We report at this time our work in this area on the radical *N*-*p*-anisyl-*N*-*tert*-butylnitroxide (**1**) which was



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chosen for study because it possesses several desirable features. The nitroxide is monomeric and has an infinite lifetime.[4] The *tert*-butyl hydrogens yield a small or zero

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