

(12 mmol) in dichloromethane (70 mL) and sodium hydroxide (125 mmol) in water (25 mL) were stirred at reflux for 48 h. The organic phase was washed with water (10 mL, 2 times), dried ( $\text{Na}_2\text{SO}_4$ ), concentrated in vacuo, yielding crystalline 7. Recrystallization from hexane/benzene gave pure 7, mp 103 °C, in 85% yield: IR  $\nu_{\text{P}=\text{O}}$  1190  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.05–7.3 (m, 10 H,  $\text{C}_6\text{H}_5$ ), 3.03–1.67 (m, 10 H), 1.53 (s, 3 H,  $\text{CH}_3$ );  $^{31}\text{P}$  NMR  $\delta$  32.63.

**(3-Oxobutyl)diphenylphosphine Oxide (8).** Oxidation of 7 (1.4 g, 4.69 mmol) by the same procedure as for 1 gave 8 as an oily residue, which was chromatographed (silica gel, chloroform:methanol, 95:5) to pure 8 as a viscous oil in 79% yield: IR (film)  $\nu_{\text{C}=\text{O}}$  1712  $\text{cm}^{-1}$ ,  $\nu_{\text{P}=\text{O}}$  1180  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR 8.0–7.3 (m, 10 H,  $\text{C}_6\text{H}_5$ ), 3.1–2.23 (m, 4 H), 2.13 (s, 3 H,  $\text{CH}_3$ );  $^{31}\text{P}$  NMR  $\delta$  32.43.

**[4,4-(Dithiotrimethylene)pentyl]triphenylphosphonium Nitrate (12).** This compound was prepared from the bromide according to a method already described<sup>4</sup> and recrystallized from chloroform/ethylacetate (10:90): yield 93%; mp 109 °C;  $^1\text{H}$  NMR  $\delta$  8.13–7.57 (m, 15 H,  $\text{C}_6\text{H}_5$ ), 4–3.33 (m, 2 H,  $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_2$ ), 3.33–1.55 (m, 10 H), 1.43 (s, 3 H,  $\text{CH}_3$ ).

**(4-Oxopentyl)triphenylphosphonium Nitrate (13).** Oxidation of 12 (1.5 g, 2.9 mmol) by the same procedure as for 1 gave crystalline 13. Recrystallization from chloroform/ethyl acetate (10:90) gave pure 13, mp 185 °C, in 85% yield: IR  $\nu_{\text{C}=\text{O}}$  1712  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.1–7.53 (m, 15 H,  $\text{C}_6\text{H}_5$ ), 3.9–3.27 (m, 2 H,  $(\text{C}_6\text{H}_5)_3\text{P}^+\text{CH}_2$ ), 3.17–2.77 (m, 2 H), 2.16 (s, 3 H,  $\text{CH}_3$ ), 2.27–1.60 (m, 2 H).

**Electrochemical Oxidation of Salts 3a–c.** Electrochemical equipment and techniques have been described elsewhere.<sup>4</sup> A solution of salt 3 (2 mmol) and tetraethylammonium nitrate (10 mmol) in  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ , 90:10 (100 mL), was oxidized at 1.5 V until the current had decayed to 10% of its initial value. The reaction mixture was concentrated and diluted with chloroform (200 mL), and the organic phase washed with water (30 mL, 3 times), dried ( $\text{Na}_2\text{SO}_4$ ), concentrated in vacuo to about 20 mL, and added dropwise to ether (200 mL). The precipitate was dried ( $\text{P}_2\text{O}_5$ , 80 °C, 1–2 torr, 24 h) to give 4a, yield 82%, 4b, yield 64%, and 4c, yield 58%.

**Registry No.** 1a ( $\text{X}^- = \text{BF}_4^-$ ), 89637-26-3; 1a ( $\text{X}^- = \text{Br}^-$ ), 71864-06-7; 1a', 89637-31-0; 1b ( $\text{X}^- = \text{BF}_4^-$ ), 89637-27-4; 1b ( $\text{X}^- = \text{Br}^-$ ), 71864-07-8; 1b', 89637-32-1; 1c ( $\text{X}^- = \text{BF}_4^-$ ), 89637-28-5; 1c ( $\text{X}^- = \text{Br}^-$ ), 80799-65-1; 1c', 89637-33-2; 1d ( $\text{X}^- = \text{BF}_4^-$ ), 89637-29-6; 1d ( $\text{X}^- = \text{Br}^-$ ), 72641-24-8; 1d', 89637-34-3; 1e ( $\text{X}^- = \text{BF}_4^-$ ), 89637-30-9; 1e ( $\text{X}^- = \text{Br}^-$ ), 72641-25-9; 1e', 89637-35-4; 2a, 43064-87-5; 2a', 43101-01-5; 2b, 89637-36-5; 2b', 85067-01-2; 2c, 89637-37-6; 2c', 85067-05-6; 2d, 89637-38-7; 2d', 85067-07-8; 2e, 89637-39-8; 2e', 85067-09-0; 3a, 85066-89-3; 3b, 85082-15-1; 3c, 89637-41-2; 4a, 89637-43-4; 4b, 89637-45-6; 4c, 89637-47-8; 5a, 89637-48-9; 5b, 89655-99-2; 5c, 89637-49-0; 6a, 72641-41-9; 7, 87177-89-7; 8, 67217-31-6; 9, 79032-15-8; 10, 35171-92-7; 11, 123-19-3; 12, 89637-51-4; 13, 89637-53-6; CAN, 16774-21-3; sodium fluoroborate, 13755-29-8; lithium perchlorate, 7791-03-9; benzaldehyde, 100-52-7.

## Synthesis of Pyrrolyl Sulfides

Masatoshi Kakushima\* and Richard Frenette

Merck Frosst Canada Inc., Pointe Claire/Dorval, Quebec, Canada H9R 4P8

Received November 22, 1983

Recently we<sup>1,2</sup> and others<sup>3</sup> have reported that *N*-(phenylsulfonyl)pyrrole (1a)<sup>4</sup> is a valuable substrate in electrophilic substitution reactions, in particular, for the regioselective introduction of acyl groups at the 3-position. In a continuation of studies on electrophilic substitution

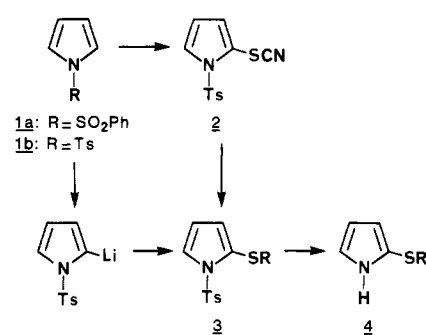
(1) Rokach, J.; Hamel, P.; Kakushima, M.; Smith, G. M. *Tetrahedron Lett.* 1981, 22, 4901.

(2) Kakushima, M.; Hamel, P.; Frenette, R.; Rokach, J. *J. Org. Chem.* 1983, 48, 3214.

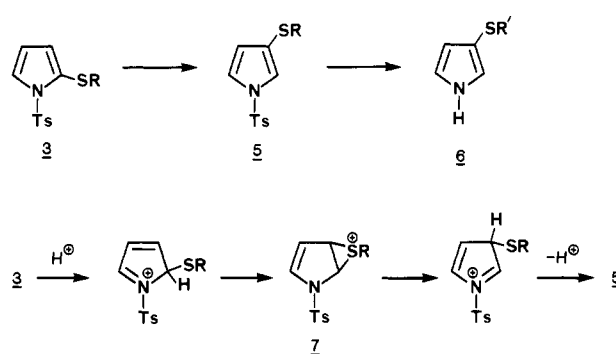
(3) Xu, R. X.; Anderson, H. J.; Gogan, N. J.; Loader, C. E.; McDonald, R. *Tetrahedron Lett.* 1981, 22, 4899.

(4) Papadopoulos, E. P.; Haider, N. F. *Tetrahedron Lett.* 1968, 1721.

Scheme I



Scheme II



of the *N*-(arylsulfonyl)pyrrole nucleus, we have explored the reactions with sulfur electrophiles, with the ultimate objective being to devise a general method for the preparation of rare 3-pyrrolyl sulfides.<sup>5</sup> In contrast to the facile 3-acylations, all attempts to introduce sulfur electrophiles directly at the 3-position of 1 failed (e.g., reaction of 1 with benzenesulfonyl chloride yielded a complex mixture). However, we have found a useful alternative method in which 3-pyrrolyl sulfides may be synthesized from readily available *N*-tosyl-2-pyrrolyl sulfides 3.

The 2-pyrrolyl sulfides 3 were prepared by the following two procedures (Scheme I): (1) *N*-tosylpyrrole (1b)<sup>4</sup> was thiocyanated with  $\text{ClSCN}$  by using conventional methods<sup>6</sup> to afford a 69% yield of the 2-(thiocyanato)pyrrole 2,<sup>7</sup> which on treatment with alkyl halides in aqueous NaOH and *tert*-butyl alcohol<sup>8</sup> gave essentially quantitative yields of 2-alkylthiopyrroles 3. (2) The 2-phenylthio derivative 3f was obtained in 70% yield from 1b, when 1b was metalated<sup>9,10</sup> with *n*-BuLi in THF for 5 min and subsequently reacted with  $\text{PhSSO}_2\text{Ph}$ <sup>11</sup> at –40 °C for 1 h. Alkaline hydrolysis of 3 afforded 1-H-2-pyrrolyl sulfides 4 in excellent yields.

In a key observation, it was found that the 3-thiosubstituted pyrroles 5 are readily available from 3 by isomerization with trifluoroacetic acid (TFA): 3 rearranges cleanly to 5 with a 1:1 mixture of TFA and 1,2-dichloro-

(5) DeSales, J.; Greenhouse, R.; Muchowski, J. M. *J. Org. Chem.* 1982, 47, 3668.

(6) Olsen, R. K.; Snyder, H. R. *J. Org. Chem.* 1963, 28, 3050.

(7) No product derived from thiocyanation at the 3-position of 1b could be detected in the crude reaction mixture. When 1b was reacted with  $(\text{SCN})_2$  in dichloromethane in the presence of  $\text{AlCl}_3$  (2 equiv), 2,5-bis(thiocyano)-*N*-tosylpyrrole, mp 130–132 °C, was obtained along with 2.

(8) When this reaction was carried out in methanol instead of *tert*-butyl alcohol, the 2-methylthio derivative 3 (R = Me, mp 64–66 °C) was produced as the byproduct. This behavior in the case of other (thiocyano)pyrroles was observed elsewhere: Olsen, R. K.; Snyder, H. R. *J. Org. Chem.* 1965, 30, 187.

(9) Hasan, I.; Marinelli, E. R.; Lin, L.-C. C.; Fowler, F. W.; Levy, A. B. *J. Org. Chem.* 1981, 46, 157.

(10) Engman, L.; Cava, M. P. *Organometallics* 1982, 1, 470.

(11) Shine, H. J.; Rahman, M.; Seeger, H.; Wu, G.-S. *J. Org. Chem.* 1967, 32, 1901.

Table I. Preparation of 3-Pyrrolyl Sulfides

precursor	R	product	mp (°C)	yield, <sup>a</sup> %	R'	3-pyrrolyl sulfide	mp (°C)	yield, <sup>a</sup> %
3a	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	5a <sup>b</sup>		55	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OMe <sup>c</sup>	6a		72
3b	CH <sub>2</sub> CO <sub>2</sub> Et	5b		87	CH <sub>2</sub> CO <sub>2</sub> H	6b	59-60	94
3c	CH <sub>2</sub> CO <sub>2</sub> H	5c <sup>b</sup>	89-90	83 <sup>d</sup>	CH <sub>2</sub> CO <sub>2</sub> H	6b		(not done)
3d	CH <sub>2</sub> Ph	5d <sup>b</sup>	82-84	85	CH <sub>2</sub> Ph	6d <sup>s</sup>		90
3e	CH <sub>2</sub> Ph- <i>p</i> -Br	5e <sup>b</sup>	105-106	84	CH <sub>2</sub> Ph- <i>p</i> -Br	6e	59-60	90
3f	Ph	5f <sup>b</sup>	80-82	60	Ph	6f <sup>s</sup>	46-48 <sup>e</sup>	98

<sup>a</sup> Isolated yields. <sup>b</sup> Satisfactory combustion analyses ( $\pm 0.3\%$  for C, H, N, and S) were obtained for these products.

<sup>c</sup> Concomitant conversion to the methyl ether occurred during the hydrolysis. <sup>d</sup> Complete isomerization after 4 h. <sup>e</sup> Lit.<sup>5</sup> mp 48.5-49.5 °C.

ethane at reflux temperature (Scheme II). This is in direct contrast to the cases of nondeactivated (alkylthio)pyrroles (e.g., 3-(benzylthio)pyrrole (6d) upon treatment with TFA is reported to give an approximately 2:1 mixture of 2- and 3-isomers at 20 °C).<sup>5</sup> <sup>1</sup>H NMR spectroscopy showed that the conversion of 3 to 5 went to completion within several hours. The rearranged products 5 were readily purified and isolated in good yields. The removal of the N-substituent from 5 was effected cleanly in basic aqueous methanol at reflux temperature to afford 1-*H*-3-pyrrolyl sulfides 6. Table I summarizes the results of the two-step synthesis of 1-*H*-3-pyrrolyl sulfides 6.

The exclusive formation of 5 with TFA deserves comment. When we carried out the isomerization of 3b to 5b in the presence of 2 equiv of *N*-(phenylsulfonyl)pyrrole (1a), neither crossover product nor 1b could be detected in the crude reaction mixture. This and the fact that no dialkyl disulfide could be detected in any of the isomerization reactions reported in Table I suggest that the conversion of 3 to 5 is intramolecular in nature and could proceed through the episulfonium salt 7 subsequent to protonation at C-2.

In view of the instability of 6 under acidic conditions, this methodology compares well with other preparations of pyrrolyl sulfides<sup>5</sup> and has the advantage of providing stable products.

### Experimental Section

Melting points were determined with an Electrothermal melting point apparatus and are uncorrected. NMR spectra were obtained with a Varian EM-390 spectrometer with Me<sub>4</sub>Si as an internal standard. Infrared spectra were recorded with a Perkin-Elmer 267 grating infrared spectrophotometer. Elemental analyses were obtained from Guelph Chemical Laboratories Ltd. Mass spectra were obtained from Morgan Schaffer. *N*-(Phenylsulfonyl)pyrrole (1a) and *N*-tosylpyrrole (1b) were prepared according to a literature method.<sup>4</sup>

***N*-Tosyl-2-(thiocyanato)pyrrole (2).** A solution of thiocyanogen chloride was prepared by adding potassium thiocyanate (8.2 g, 83 mmol) in one portion to a solution of chlorine (5.5 g, 78 mmol) in 200 mL of glacial acetic acid. The resulting solution was stirred for 0.5 h at room temperature and was rapidly added to a solution of 1b (4.4 g, 20 mmol) in 100 mL of glacial acetic acid in an atmosphere of nitrogen. The reaction mixture was stirred at room temperature for 0.5 h and poured into 2 L of cold water, and the product was extracted into dichloromethane. Removal of the solvent and chromatography of the residue on silica gel, eluting with 1:5 ethyl acetate-hexane, afforded 2: 3.84 g (69%); mp 93-95 °C; IR (KBr) 2163, 1598, 1372, 1173, 1153 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.45 (3 H, s), 6.40 (1 H, t,  $J = 3.0$  Hz), 6.80 (1 H, m), 7.43 and 7.93 (4 H, AB q,  $J = 8$  Hz), 7.67 (1 H, m); MS,  $m/z$  278 (M<sup>+</sup>). Anal. Calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 51.78; H, 3.62; N, 10.07; S, 23.04. Found: C, 51.81; H, 3.54; N, 10.04; S, 23.02.

**General Procedure for the Transformation of 2 to 3.** To a mixture of 2 (1.27 g, 4.57 mmol) and 1,3-dibromopropane (1.4 mL, 13.7 mmol) in 45 mL of *tert*-butyl alcohol was added 1 N NaOH (13.7 mL, 13.7 mmol). The resulting solution was stirred at room temperature for 2.5 h and diluted with water. The mixture was acidified with 1 N HCl and extracted with di-

chloromethane. Removal of the solvent and chromatography of the residue on silica gel, eluting with 3:20 ethyl acetate-hexane, afforded *N*-tosyl-2-[(3-bromopropyl)thio]pyrrole (3a): 1.39 g (81%); mp 35-37 °C; IR (KBr) 1600, 1365, 1175, 1155 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.10 (2 H, m), 2.40 (3 H, s), 2.85 (2 H, t,  $J = 7$  Hz), 3.45 (2 H, t,  $J = 7$  Hz), 6.25 (1 H, t,  $J = 3$  Hz), 6.37 (1 H, m), 7.35 and 7.90 (4 H, AB q,  $J = 8$  Hz), 7.57 (1 H, m); MS,  $m/z$  373 and 375 (M<sup>+</sup>). Anal. Calcd for C<sub>14</sub>H<sub>16</sub>BrNO<sub>2</sub>S<sub>2</sub>: C, 44.92; H, 4.31; N, 3.74; S, 17.13. Found: C, 44.84; H, 4.34; N, 3.76; S, 17.13.

**Ethyl [(*N*-tosyl-2-pyrrolyl)thio]acetate (3b):** 94%; mp 56-58 °C; IR (KBr) 1735, 1600, 1365, 1175, 1155 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.25 (3 H, t), 2.45 (3 H, s), 3.45 (3 H, s), 4.20 (2 H, q), 6.25 (1 H, t,  $J = 3$  Hz), 6.55 (1 H, m), 7.35 and 7.90 (4 H, AB q,  $J = 8$  Hz), 7.60 (1 H, m); MS,  $m/z$  339 (M<sup>+</sup>). Anal. Calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>4</sub>S<sub>2</sub>: C, 53.07; H, 5.05; N, 4.13; S, 18.89. Found: C, 53.02; H, 5.00; N, 4.16; S, 18.58.

***N*-Tosyl-2-(benzylthio)pyrrole (3d):** 96%; mp 82-84 °C; IR (KBr) 1600, 1365, 1175, 1155 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.40 (3 H, s), 3.90 (2 H, s), 6.05-6.20 (2 H, m), 7.10-7.40 (7 H, m), 7.52 (1 H, m), 7.90 (2 H, d,  $J = 8$  Hz); MS,  $m/z$  343 (M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>S<sub>2</sub>: C, 62.94; H, 4.99; N, 4.08; S, 18.67. Found: C, 62.82; H, 4.95; N, 4.04; S, 18.58.

***N*-Tosyl-2-[(*p*-bromobenzyl)thio]pyrrole (3e):** 98%; mp 75-77 °C; IR (KBr) 1600, 1365, 1175, 1155 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.45 (3 H, s), 3.90 (3 H, s), 6.10-6.30 (2 H, m), 7.00 (2 H, d,  $J = 8$  Hz), 7.30-7.50 (4 H, m), 7.60 (1 H, m), 7.95 (2 H, d,  $J = 8$  Hz); MS,  $m/z$  421 and 423 (M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>BrNO<sub>2</sub>S<sub>2</sub>: C, 51.18; H, 3.82; N, 3.32; S, 15.18. Found: C, 50.93; H, 4.01; N, 3.48; S, 15.04.

**General Procedure for the Hydrolysis of 3.** A mixture of 3b (300 mg, 0.885 mmol), 2.7 mL of 2 N NaOH, and 8 mL of methanol was refluxed for 8 h and diluted with water. The mixture was acidified with 1 N HCl and the product was extracted into ethyl acetate. Removal of the solvent and chromatography of the residue on silica gel, eluting with 1:20:100 acetic acid-dioxane-toluene, afforded the known (2-pyrrolylthio)acetic acid (4, R = CH<sub>2</sub>CO<sub>2</sub>H)<sup>12</sup> as an oil: 130 mg (93%); IR (film) 3500-2500, 3380, 1715, 1410 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.40 (2 H, s), 4.95 (2 H, br, exchangeable with D<sub>2</sub>O), 6.20 (1 H, m), 6.45 (1 H, m), 6.90 (1 H, m). Anal. Calcd for C<sub>6</sub>H<sub>7</sub>NO<sub>2</sub>S: C, 45.84; H, 4.49; N, 8.91; S, 20.40. Found: C, 45.79; H, 4.68; N, 8.78; S, 20.43.

**[(*N*-Tosyl-2-pyrrolyl)thio]acetic Acid (3c).** A mixture of 3b (100 mg, 0.294 mmol), 1 mL of ethanol, and 0.22 mL of 2 N NaOH was stirred at room temperature for 1 h. The mixture was diluted with water, acidified with 1 N HCl, and extracted with ethyl acetate. Removal of the solvent gave 3c: 87 mg (96%); mp 133-135 °C; IR (KBr) 3500-2500, 1700, 1365, 1170, 1150 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.45 (3 H, s), 3.55 (2 H, s), 6.30 (1 H, t,  $J = 3$  Hz), 6.60 (1 H, m), 6.65 (1 H, m), 7.40 and 7.95 (4 H, AB q,  $J = 8$  Hz). Anal. Calcd for C<sub>13</sub>H<sub>13</sub>NO<sub>4</sub>S<sub>2</sub>: C, 50.14; H, 4.21; N, 4.50; S, 20.60. Found: C, 50.18; H, 4.29; N, 4.21; S, 20.12.

***N*-Tosyl-2-(phenylthio)pyrrole (3f).** To a solution of 1b (330 mg, 1.5 mmol) in 10 mL of THF at -15 °C was added *n*-BuLi (1.6M in hexane; 1.1 mL, 1.76 mmol) in an atmosphere of N<sub>2</sub>. The mixture was stirred at -15 °C for 5 min and cooled to -78 °C, and a solution of PhSSO<sub>2</sub>Ph (400 mg, 1.6 mmol) in 3 mL of THF was added. The mixture was stirred at -40 °C for 1 h. The

(12) Matteson, D. A.; Snyder, H. R. *J. Org. Chem.* 1957, 22, 1500. See also: Gronowitz, S.; Hörnfeldt, A.; Gestblom, B.; Hoffman, R. A. *Arkiv. Kemi* 1961, 18, 151.

reaction was quenched with brine, and the product was extracted into ether. Removal of the solvent and chromatography of the residue on silica gel, eluting with 1:10 ethyl acetate-hexane, afforded **3f**: 340 mg (70%); mp 104-105 °C; IR (KBr) 1600, 1363, 1175, 1155 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.30 (3 H, s), 6.36 (1 H, t, *J* = 3 Hz), 6.70 (1 H, m), 6.77-6.87 (2 H, m), 7.00-7.13 (5 H, m), 7.65 (1 H, m), 7.73 (2 H, d, *J* = 8 Hz). Anal. Calcd for C<sub>17</sub>H<sub>15</sub>NO<sub>2</sub>S<sub>2</sub>: C, 61.98; H, 4.59; N, 4.25; S, 19.47. Found: C, 61.88; H, 4.53; N, 4.56; S, 19.35.

**General Procedure for the Isomerization of 3 to 5.** A mixture of **3b** (660 mg, 1.95 mmol), 5 mL of 1,2-dichloroethane, and 5 mL of TFA was refluxed for 2.5 h. Removal of the solvent and chromatography of the residue on silica gel, eluting with 1:5 ethyl acetate-hexane, afforded ethyl [(*N*-tosyl-3-pyrrolyl)thio]acetate (**5b**): 576 mg (87%); IR (film) 1735, 1600, 1370, 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.20 (3 H, t), 2.45 (3 H, s), 3.40 (2 H, s), 4.15 (2 H, q), 6.35 (1 H, m), 7.17 (1 H, m), 7.30 (1 H, m), 7.35 and 7.80 (4 H, AB q, *J* = 8 Hz). Anal. Calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>2</sub>S<sub>2</sub>: C, 53.07; H, 5.05; N, 4.13; S, 18.89. Found: C, 53.18; H, 5.26; N, 4.37; S, 18.88.

**General Procedure for the Hydrolysis of 5.** A mixture of **5b** (396 mg, 1.17 mmol), 20 mL of methanol, and 2.9 mL of 2 N NaOH was refluxed for 2 h. The mixture was cooled, diluted with water and acidified (pH 6) with 1 N HCl, and extracted with ethyl acetate. Removal of the solvent afforded (3-pyrrolylthio)acetic acid (**6b**): 173 mg (94%); mp 59-60 °C; IR (KBr) 3380, 3300-2500, 1710 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.35 (2 H, s), 6.27 (1 H, m), 6.73 (1 H, m), 6.92 (1 H, m), 9.6-10.4 (2 H, exchangeable with D<sub>2</sub>O). Anal. Calcd for C<sub>6</sub>H<sub>7</sub>NO<sub>2</sub>S: C, 45.84; H, 4.49; N, 8.91; S, 20.40. Found: C, 45.90; H, 4.52; N, 8.81; S, 20.14.

**3-[(3-Methoxypropyl)thio]pyrrole (6a):** IR (film) 3500-3100, 2930, 1110 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.85 (2 H, quintet, *J* = 7 Hz), 2.75 (2 H, t, *J* = 7 Hz), 3.35 (3 H, s), 3.50 (2 H, t, *J* = 7 Hz), 6.27 (1 H, m), 6.70-6.90 (2 H, m), 8.20-8.90 (1 H, exchangeable with D<sub>2</sub>O).

**3-[(*p*-Bromobenzyl)thio]pyrrole (6e):** mp 59-60 °C; IR (KBr) 3370, 1490, 1070 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.80 (2 H, s), 6.20 (1 H, m), 6.70 (1 H, m), 6.80 (1 H, m), 7.10 and 7.45 (4 H, AB q, *J* = 8 Hz), 8.0-8.5 (1 H, exchangeable with D<sub>2</sub>O). Anal. Calcd for C<sub>11</sub>H<sub>10</sub>BrNS: C, 49.26; H, 3.76; N, 5.22; S, 11.96. Found: C, 49.30; H, 3.68; N, 5.17; S, 11.63.

**Isomerization of 3b to 5b in the Presence of 1a.** A solution of **1a** (42 mg, 0.20 mmol) and **3b** (34 mg, 0.10 mmol) in 1 mL each of 1,2-dichloroethane and TFA was refluxed for 2 h. The mixture was cooled and concentrated to dryness. Chromatography of the residue on silica gel, eluting with 3:10 ethyl acetate-hexane, afforded 22 mg (65%) of **5b** and 40 mg of **1a**.

**Acknowledgment.** We thank Drs. J. G. Atkinson and R. N. Young for valuable discussions and Mr. P. Hamel for providing us with quantities of **1b**.

**Registry No.** **1b**, 17639-64-4; **2**, 89597-62-6; **3a**, 89597-63-7; **3b**, 89597-64-8; **3c**, 89597-65-9; **3d**, 89597-66-0; **3e**, 89597-67-1; **3f**, 89597-68-2; **4** (R = CH<sub>2</sub>CO<sub>2</sub>H), 89597-78-4; **5a**, 89597-69-3; **5b**, 89597-70-6; **5c**, 89597-71-7; **5d**, 89597-72-8; **5e**, 89597-73-9; **5f**, 89597-74-0; **6a**, 89597-75-1; **6b**, 89597-76-2; **6d**, 82511-51-1; **6e**, 89597-77-3; **6f**, 82511-49-7; 1,3-dibromopropane, 109-64-8.

### Redox Properties of Some Novel Cumulene Electron Donors. Electrodimerization and Stability of Heterocumulene Cation Radicals

Franklin D. Saeva,\* Jeffrey J. Doney, and Bradley P. Morgan

Research Laboratories, Eastman Kodak Company,  
Rochester, New York 14650

Received October 12, 1983

There has been considerable interest recently in organic polymers<sup>1</sup> and crystals<sup>2</sup> that show "metal-like" conduc-

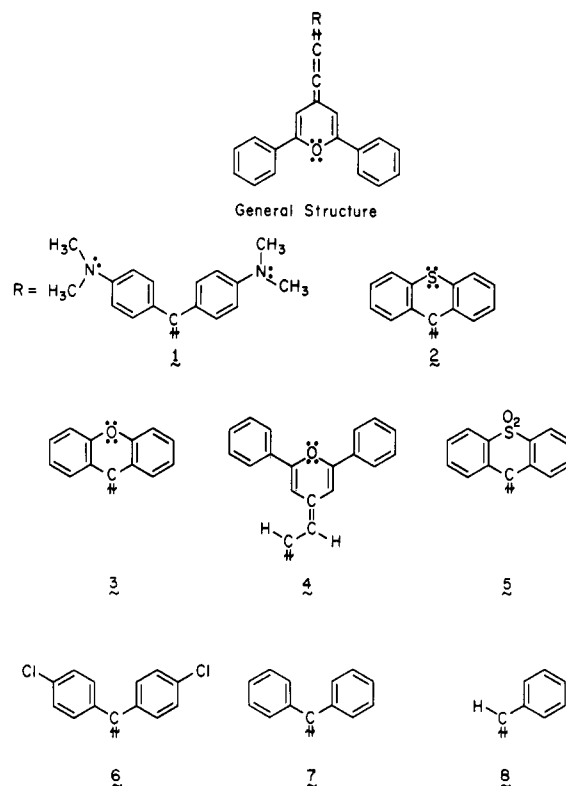
Table I. Electrochemical Behavior of Some Cumulene Derivatives<sup>a</sup>

compd	<i>E</i> <sub>1</sub> <sup>o'</sup>		rev	<i>E</i> <sub>2</sub> <sup>o'</sup>		rev	<i>E</i> <sub>2</sub> <sup>o'</sup> - <i>E</i> <sub>1</sub> <sup>o'</sup>
	<i>E</i> <sub>p</sub> <sup>a</sup>	<i>E</i> <sub>p</sub> <sup>c</sup>		<i>E</i> <sub>p</sub> <sup>a</sup>	<i>E</i> <sub>p</sub> <sup>c</sup>		
1	0.14	0.07	rev	0.30	0.24	rev	0.16
2	0.44	0.38	rev	0.76	0.70	rev	0.32
3	0.46	0.40	rev	0.83	0.76	rev	0.37
4	0.27	0.19	rev	0.41	0.33	rev	0.14
5	0.83	0.75	rev				
6	0.69	0.62	rev				
7	0.66 <sup>b</sup>		irrev				
8	0.76 <sup>b</sup>		irrev				

<sup>a</sup> V vs. SCE, 0.1 N tetrabutylammonium fluoroborate electrolyte in methylene chloride, cyclic voltammetry at -80 °C, *c* = 1.0 × 10<sup>-4</sup> M cumulene, 0.5 V/s scan rate, SCE reference electrode, glassy carbon working electrode. *E*<sub>p</sub><sup>a</sup> and *E*<sub>p</sub><sup>c</sup> refer to peak potentials for anodic and cathodic waves, respectively. <sup>b</sup> *E*<sub>p</sub> at 200 mV s<sup>-1</sup> scan rate.

tivity. Electronic conductivity in the organic crystals requires the formation of segregated columns of an electron donor, e.g., tetrathiafulvalene (TTF), and an electron acceptor, e.g., 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), as well as partial charge transfer between the donor (D) and the acceptor (A). Novel electron donors and acceptors are being synthesized with the hope of finding the proper combination of D and A or D alone that will produce crystals with superconducting properties at atmospheric pressure and room temperature.<sup>3</sup>

We report the redox behavior of a novel class of electron donors, the cumulenes. The cumulenes 1-8 have a planar



structure and low oxidation potentials and form stable cation radicals when properly substituted. The cumulenes are a new class of electron-donor partners that may be used with the appropriate electron acceptors to form charge-transfer salts.<sup>4,5</sup>

(2) Perlstein, J. *Angew. Chem, Int. Ed. Engl.* 1977, 16, 519.  
(3) Wudl, F. *Pure Appl. Chem.* 1982, 54, 1051.

(1) Wegner, G. *Angew. Chem.* 1981, 93, 352.