

## Reaction of 2-Nitrothiophen with Secondary Aliphatic Amines

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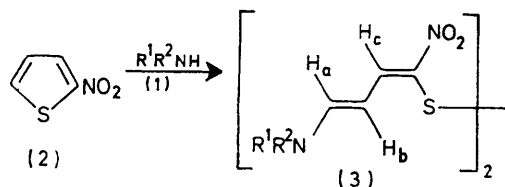
Secondary aliphatic amines react with 2-nitrothiophen in ethanol at room temperature to yield bis-(4-dialkylamino-1-nitrobuta-1,3-dienyl) disulphides. The disulphide is shown to be generated *via* the preliminary formation of the corresponding thiol. A mechanism involving nucleophilic attack by the amine at the 5 position of the nitro-activated thiophen ring, and proton transfer to yield a sulphonium-type intermediate followed by ring-opening, is proposed.

THE formation of adducts from the reversible addition of bases (alkoxides, amines, carbanions, *etc.*) to nitro-activated aromatic compounds continues to be of interest.<sup>1</sup> The reactivity of alkoxides toward a variety of nitro-activated aromatic substrates has been thoroughly investigated,<sup>1,2</sup> while studies on the reactivity of other bases toward aromatic compounds have been mainly confined to the reactions of dinitro- and trinitro-benzene derivatives.<sup>1,3</sup>

In continuation of our studies on thiophen derivatives,<sup>4</sup> we now report on the reactions of 2-nitrothiophen with some secondary aliphatic amines.

### RESULTS AND DISCUSSION

The aliphatic secondary amines (1a—e) react readily with 2-nitrothiophen (2) in ethanol at room temperature to yield bis-(4-dialkylamino-1-nitrobuta-1,3-dienyl) disulphides (3a—e). The readiness of the reaction is



- a;  $R^1 = R^2 = \text{Me}$   
 b;  $R^1 = R^2 = \text{Et}$   
 c;  $R^1 = R^2 = \text{Pr}^n$   
 d;  $R^1R^2N = \text{C}_5\text{H}_{10}\text{N}$  (piperidino)  
 e;  $R^1R^2N = \text{C}_4\text{H}_8\text{ON}$  (morpholino)

indicated by the almost instantaneous development of a bright red colour on addition of a solution of the amine in ethanol to 2-nitrothiophen dissolved in the same solvent. Keeping the reaction mixture at 0° for 8—10

<sup>1</sup> G. Briegleb, 'Elektronen Donator-Akzeptor Komplexe,' Springer Verlag, Berlin, 1961; J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, Amsterdam, 1968; E. Bunzel, A. R. Norris, and K. E. Russel, *Quart. Rev.*, 1968, **22**, 123; F. Pietra, *Quart. Rev.*, 1969, **23**, 504; P. Buck, *Angew. Chem. Internat. Edn.*, 1969, **8**, 120; M. Crampton, *Adv. Phys. Org. Chem.*, 1969, **7**, 211; R. Foster, 'Organic Charge-transfer Complexes,' Academic Press, New York, 1969; M. J. Strauss, *Chem. Rev.*, 1970, **70**, 667; M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1973, 1103, and references therein; J. W. Larsen, K. Amin, S. Ewing, and L. L. Magid, *J. Org. Chem.*, 1972, **37**, 3857; G. Biggi and F. Pietra, *J.C.S. Perkin I*, 1973, 1980; M. P. Simounin, M. J. Lecourt, F. Terrier, and C. A. Dearing, *Canad. J. Chem.*, 1972, **50**, 3558.

<sup>2</sup> D. Spinelli, V. Armanino, and A. Corrao, *J. Heterocyclic Chem.*, 1970, **7**, 1441; G. Doddi, G. Illuminati, and F. Stegel, *J.C.S. Chem. Comm.*, 1972, 1143; *Tetrahedron Letters*, 1973, 3221; C. Paulmier, M. P. Simounin, A. P. Chatrousse, and F. Terrier, *ibid.*, p. 1123; G. Biggi, C. A. Veracini, and F. Pietra, *J.C.S. Chem. Comm.*, 1973, 523; T. Abe and T. Asao, *Tetrahedron Letters*, 1973, 1327; F. De Santis and F. Stegel, *Gazzetta*, 1973, 649.

days results in the precipitation of red crystals of the product (50—80% yields). T.l.c. analysis of the product isolated by filtration indicates that it is not accompanied by by-products. Compounds (3a—e) were identified on the basis of their elemental analyses, and i.r. and <sup>1</sup>H n.m.r. spectra (see Experimental section). For example, the n.m.r. spectrum of (3b) in CDCl<sub>3</sub> showed one-proton signals at  $\tau$  1.76 (d,  $J$  12.3 Hz), 2.79 (d,  $J$  12.3 Hz), and 4.33 (t,  $J$  12.3 Hz), assigned to the protons originally attached to C(3), C(5), and C(4) of the thiophen skeleton respectively. The spectra of the products from reaction of diethylamine with 2-nitro-3-deuterio- and with 2-nitro-5-deuterio-thiophen (see Experimental section) confirmed that these assignments were correct. The appearance of the H<sub>b</sub> signal as a triplet is due to the fact that  $J_{ab}$  and  $J_{bc}$  values are equal (12.3 Hz). The value of  $J_{ab}$  is near the lower limit of the range expected<sup>5</sup> (11—18 Hz) for  $J_{trans}$ . However, a strong band at 985 cm<sup>-1</sup> in the i.r. spectrum of (3b) leaves no doubt concerning its *trans*-HC=CH- configuration.<sup>6</sup> The nature of the 1- and 4-substituents (NO<sub>2</sub> and NR<sub>2</sub>) of the butadiene system in (3) might be responsible for the low value of  $J_{trans}$ . The value of  $J_{bc}$  indicates a torsion angle of 180° between the C-H bonds.<sup>5</sup> The planarity of the butadiene system is also suggested by the relatively low value ( $\tau$  4.33) of the chemical shift of H<sub>b</sub>: appreciable twisting

<sup>3</sup> M. R. Crampton and V. Gold, *J. Chem. Soc. (B)*, 1967, 23, and references therein; A. K. Dwivedy, D. B. Parihar, S. P. Sharma, and K. K. Verma, *J. Chromatog.*, 1967, **29**, 120; R. E. Miller and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 1961, 4886; 1959, 2375; *Nature*, 1960, **186**, 149; R. Foster and D. Ll. Hammick, *J. Chem. Soc.*, 1954, 2685; R. Foster and R. K. Mackie, *ibid.*, 1962, 3843; R. Foster and J. W. Morris, *J. Chem. Soc. (B)*, 1970, 703; R. Foster and C. A. Five, *Rev. Pure Appl. Chem. (Australia)*, 1966, **16**, 61; W. Liptay and N. Tamberg, *Z. Elektrochem.*, 1962, **66**, 59; C. R. Allen, A. J. Brook, and E. F. Caldin, *J. Chem. Soc.*, 1961, 2171; C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1970, **92**, 129.

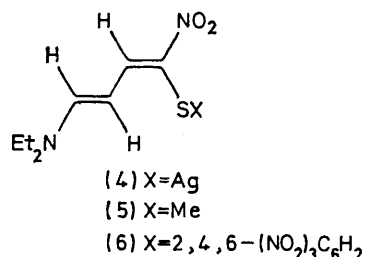
<sup>4</sup> Preliminary communication, G. Guanti, C. Dell'Erba, and G. Leandri, *J.C.S. Chem. Comm.*, 1972, 1060; D. Spinelli, G. Guanti, and C. Dell'Erba, *J.C.S. Perkin II*, 1972, 441, and previous papers in the series; D. Spinelli, C. Dell'Erba, G. Guanti, and M. Novi, *J. Heterocyclic Chem.*, in the press; S. Gronowitz, 'Organosulfur Chemistry,' ed. M. J. Janssen, Interscience, New York, 1967, pp. 119—141; *Adv. Heterocyclic Chem.*, 1963, **1**, 1.

<sup>5</sup> P. W. Hickmott, B. J. Hopkins, and C. T. Yoxall, *J. Chem. Soc. (B)*, 1971, 205, and previous papers in the series; A. A. Bothner and R. K. Harris, *J. Amer. Chem. Soc.*, 1965, **87**, 3445, 3451; H. Braun, N. Mayer, and G. Kresze, *Annalen*, 1972, **762**, 111; G. K. Helmkamp, B. A. Olsen, and J. R. Koskinen, *J. Org. Chem.*, 1965, **30**, 1623; P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, 1970, **92**, 7631; L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon Press, Oxford, 2nd edn., 1969.

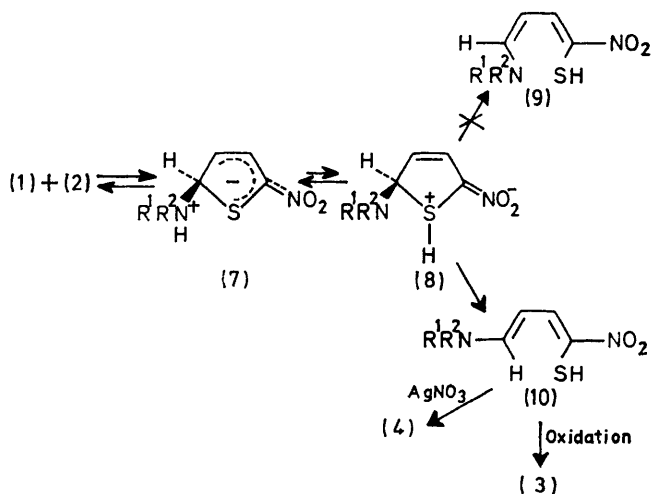
<sup>6</sup> K. Nakanishi, 'Infrared Absorption Spectroscopy—Practical,' Holden-Day, San Francisco, 1962.

of the double bonds out of the plane would result in increased electron density at C-3 and an upfield shift<sup>5</sup> of the  $H_b$  signal (to  $\tau$  5.1–5.3). Strong conjugation of the  $\text{NO}_2$  and  $\text{NR}_2$  groups across the  $\pi$ -system is evidenced by the presence of a strong band [ $\lambda_{\text{max}}$  458 nm ( $\log \epsilon$  4.75)] in the u.v. spectrum of (3b). Such conjugative interaction must confer some double bond character to the C– $\text{NR}^1\text{R}^2$  bond in (3); in fact the  $^1\text{H}$  n.m.r. spectrum of (3a) in dimethyl sulphoxide (DMSO) at 25° shows two distinct, equally intense singlets for the NMe resonances at  $\tau$  6.80 and 7.03. On warming the sample, these signals broaden and finally coalesce at ca. 70°. The  $^1\text{H}$  n.m.r. spectrum of (3b) in DMSO also show non-equivalence of the NMe groups.

The disulphides (3) most probably arise *via* preliminary formation of the corresponding thiols (or thiolate ions). Attempts to isolate these thiols have been unsuccessful, as they are readily further oxidized to disulphides. However, their intermediacy is supported by the following evidence. (i) Reaction between (2) and diethylamine in ethanol in the presence of silver nitrate leads to the isolation of silver (*Z,E*)-4-diethylamino-1-nitrobuta-1,3-diene-1-thiolate (4) identified by elemental analysis and



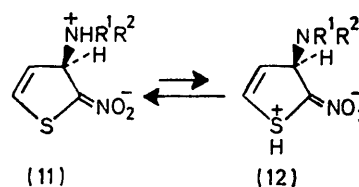
$^1\text{H}$  n.m.r. and i.r. spectra. Treatment of (4) with methyl iodide and picryl chloride gave the derivatives (5) and (6) (see Experimental section). (ii) Compound (4) can be converted into the disulphide (3) by exposing its ethanol solution to air. (iii) In the reaction of (2) with amines,



SCHEME

the rate of formation of (3) is greatly enhanced if the reaction is performed in an atmosphere of oxygen.

The mechanism in the Scheme can be proposed for the reactions described here. Nucleophilic attack by the amine on the thiophen ring would occur at the favoured position 5, yielding the intermediate (7) and hence, by way of rapid proton transfer, the sulphonium-type isomer (8); opening of the ring would then give the thiol (10). Nucleophilic attack by the amine can also occur at position 3 of 2-nitrothiophen, and treatment of (2) with metal amides in aprotic solvents results in mixtures of 2-nitro-5-amino- and 2-nitro-3-amino-thiophen.<sup>4</sup> The fact that 2-dialkylaminobuta-1,3-dienes are not observed as reaction products suggests that intermediates of the type (12) formed through (11) are unable to undergo ring opening under the reaction conditions, and that only the



reaction path in the Scheme remains open. Ring opening of the intermediate (8) should yield both the (*Z,E*)-buta-1,3-diene derivative (10) and its (*Z,Z*)-isomer (9): however, only compounds related to (10) were obtained. This stereospecificity might be rationalized by invoking greater steric interactions in the transition state leading from (8) to (9) than in passing from (8) to (10). This is not unreasonable since, during the breaking of the C–S bond involved in ring-opening, outward rotation of the  $\text{NR}^1\text{R}^2$  group should be sterically favoured.

The most intriguing point of the foregoing mechanism is the step involving the opening of the thiophen ring, and further studies on this are needed. A few other ring opening reactions of thiophen are known,<sup>4,7</sup> but its occurrence under the extremely mild conditions observed here is both unprecedented and surprising.

## EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 instrument,  $^1\text{H}$  n.m.r. spectra on a Varian XL-100-12, and u.v. spectra on a Zeiss P.M. Q II spectrophotometer. Molecular weights were determined with a Mechrolab vapour pressure osmometer.

**Materials.**—Dimethylamine, diethylamine, dipropylamine, piperidine, and morpholine were commercial (Fluka) products. 2-Nitrothiophen was prepared by the reported methods.<sup>8</sup>

**2-Deuterio-5-nitrothiophen.**—2-Bromo-5-nitrothiophen<sup>9</sup> (2 g, 9.6 mmol) was dissolved in  $\text{CH}_3\text{CO}_2\text{D}$  (8 ml) and copper powder (1.2 g, 19 mg atom) was added in portions with stirring. The mixture was heated under reflux for 30 min and filtered. The solvent was distilled off and the residue crystallized from light petroleum (b.p. 30–50°), m.p. 44–45°,  $\tau$  ( $\text{CDCl}_3$ ) 2.05 (1H, d,  $J$  4 Hz) and 2.91 (1H, d,  $J$  4 Hz). Only traces of undeuteriated compound were present.

<sup>7</sup> C. Dell'Erba, D. Spinelli, and G. Leandri, *Chem. Comm.*, 1969, 549.

<sup>8</sup> A. H. Blatt, S. Bach, and W. L. Kresch, *J. Org. Chem.*, 1957, 22, 1693; *Org. Synth.*, Coll. Vol. II, 1943, p. 466.

<sup>9</sup> D. Spinelli, C. Dell'Erba, and G. Guanti, *Ann. Chim. (Italy)*, 1965, 55, 1260.

**3-Deuterio-2-nitrothiophen.**—This compound was prepared from 3-bromo-2-nitrothiophen<sup>4</sup> following the procedure described above. Crystallization from light petroleum (b.p. 30–50°), gave the product, m.p. 44–45°,  $\tau$  (CDCl<sub>3</sub>) 2.43 (1H, d,  $J$  5.4 Hz) and 2.93 (1H, d,  $J$  5.4 Hz). Only traces of undeuteriated compound were present.

**Reaction of 2-Nitrothiophen with Diethylamine.**—Diethylamine (0.4 ml, 3.9 mmol) dissolved in ethanol (10 ml) was added dropwise to a solution of 2-nitrothiophen (0.5 g, 3.9 mmol) in ethanol (10 ml) at room temperature. The solution was kept at 0 °C for ca. 10 days. The bright red precipitate was filtered off (0.39 g, 50%) and crystallized

1430, 1340br, 1295, 1240, 1170–1120, 1080, and 990 cm<sup>-1</sup>,  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO] 1.80 (1H, d,  $J$  12 Hz), 2.25 (1H, d,  $J$  12 Hz), 4.23 (1H, t,  $J$  12 Hz), 7.02 (4H, q,  $J$  7.2 Hz, NCH<sub>2</sub>CH<sub>3</sub>), and 8.83 (6H, t,  $J$  7.2 Hz, NCH<sub>2</sub>CH<sub>3</sub>),  $\lambda_{\max}$ . (DMSO) 505 nm (log  $\epsilon$  4.42).

**Reaction of the Silver Salt (4) with Methyl Iodide.**—A mixture of (4) (2 g, 6.5 mmol) in CH<sub>3</sub>I (2 ml) was kept at room temperature for 30 min and then extracted several times with acetone. Evaporation of the solvent gave a yellow oil which solidified (1.3 g). The product crystallized from light petroleum (b.p. 30–50°)–ether to give (Z,E)-4-diethylamino-1-nitrobuta-1,3-dienyl methyl sulphide (5), m.p. 53–54 °C

TABLE 1

Analytical data of the products (3a–e) obtained from 2-nitrothiophen and secondary aliphatic amines in ethanol

	Crystallization solvent	M.p. (°C)	Found (%)				Formula	Required (%)			
			C	H	N	S		C	H	N	S
(3a)	MeNO <sub>2</sub>	144	41.5	5.25	16.2	18.5	C <sub>12</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	41.6	5.25	16.15	18.5
(3b)	Me <sub>2</sub> CO–petrol *	138	47.8	6.5	13.9	15.85	C <sub>16</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	47.75	6.5	13.9	15.95
(3c)	C <sub>6</sub> H <sub>6</sub>	154	52.3	7.4	12.2	13.85	C <sub>20</sub> H <sub>34</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	52.4	7.45	12.2	14.0
(3d)	MeCN	158	50.8	6.15	13.1	14.95	C <sub>18</sub> H <sub>26</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	50.7	6.15	13.15	15.05
(3e)	CHCl <sub>3</sub> –petrol *	160	44.65	5.1	12.9	15.0	C <sub>16</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub>	44.65	5.15	13.0	14.9

\* Light petroleum (b.p. 30–60°).

from acetone–light petroleum (b.p. 30–60°) gave a product with m.p. 138°. T.l.c. on Kieselgel G (benzene–acetone, 4 : 1) showed only one spot ( $R_F$  0.28). The product was shown to be *bis*-(4-diethylamino-1-nitrobuta-1,3-dienyl) di-sulphide (3b) on the basis of analytical and spectral data (Tables 1 and 2),  $\lambda_{\max}$ . (CHCl<sub>3</sub>) 458 nm (log  $\epsilon$  4.75).

Attempts were made to improve the yield of (3b). Adding 2-nitrothiophen (0.5 g, 3.9 mmol) to an oxygen-saturated ethanolic solution of diethylamine (2 ml; 19.5 mmol) and diethylamine hydrochloride (2.14 g, 19.5 mmol) and working up the solution as above gave product (0.63 g, ca. 80%).

The same procedure was used for other secondary aliphatic amines. The analytical and spectral data of the products (3a–e) are in Table 1 and in Table 2 respectively.

Products similar to (3b) were obtained by using diethylamine and 3-deuterio-2-nitro- and 5-deuterio-2-nitro-thiophen as substrates. The product from 3-deuterio-2-nitrothiophen had  $\tau$  (CDCl<sub>3</sub>) 2.79 (1H, d,  $J$  12.3 Hz), 4.33 (1H, d,  $J$  12.3 Hz), 6.60 (4H, d,  $J$  7.2 Hz), and 8.73 (6H, t,  $J$  7.2 Hz), and the product from 5-deuterio-2-nitrothiophen  $\tau$  (CDCl<sub>3</sub>) 1.76 (1H, d,  $J$  12.3 Hz), 4.33 (1H, d,  $J$  12.3 Hz), 6.60 (4H, q,  $J$  7.2 Hz), and 8.73 (6H, t,  $J$  7.2 Hz). Only traces of undeuteriated products were found.

**Reaction of 2-Nitrothiophen with Diethylamine in the Presence of Silver Nitrate.**—Diethylamine (5 g, 68.5 mmol) was added dropwise to a solution of AgNO<sub>3</sub> (1.4 g, 8.2 mmol) in ethanol (50 ml). A small amount of precipitate was filtered off and to the filtrate 2-nitrothiophen (1 g, 7.8 mmol) dissolved in ethanol (10 ml) was added. The solution was kept at 0 °C for ca. 10 days, and a dark red precipitate was filtered off, and washed with ethanol and anhydrous ether to give product (1.7 g). The product was purified by dissolving it in *NN*-dimethylformamide and precipitating it with ether. It decomposes on warming (ca. 140 °C) developing nitrous vapours and depositing metallic silver. Elemental analysis and spectral data showed the product to be *silver* (Z,E)-4-diethylamino-1-nitrobuta-1,3-diene-1-thiolate (4) (Found: C, 31.0; H, 4.15; N, 9.0. C<sub>8</sub>H<sub>13</sub>AgN<sub>2</sub>O<sub>2</sub>S requires C, 31.1; H, 4.25; N, 9.05%),  $\nu_{\max}$ . (Nujol) 1605, 1550br,

(Found: C, 50.0; H, 7.5; N, 13.0; S, 14.85. C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 50.0; H, 7.45; N, 12.95; S, 14.8%),  $\nu_{\max}$ . (Nujol) 1612, 1555, 1540, 1452, 1420, 1352, 1305, 1258, 1180–1160, 1120, 1105, 1080, 1060, 1015, and 990 cm<sup>-1</sup>,  $\tau$

TABLE 2

Spectral data of products (3a–e) obtained from 2-nitrothiophen and secondary aliphatic amines in ethanol

	<sup>1</sup> H n.m.r. <sup>a</sup> ( $\tau$ ; $J$ in Hz)			R	I.r. <sup>b</sup> (cm <sup>-1</sup> )
	H <sub>a</sub>	H <sub>b</sub>	H <sub>c</sub>		
(3a)	2.12 (12.1)	4.52 (12.1)	1.78 (12.1)	CH <sub>3</sub> 6.80 7.03	1620, <sup>d</sup> 1562, 1544, 1435, 1415, 1340, <sup>d</sup> 1300, 1260, <sup>d</sup> 1200, 1175, 1106, <sup>d</sup> 995
(3b) <sup>e</sup>	2.12 (12.5)	4.40 (12.5)	1.72 (12.5)	CH <sub>2</sub> <sup>e</sup> 8.80 CH <sub>3</sub> 8.80 8.85	1610, <sup>d</sup> 1545, <sup>d</sup> 1440, 1345, 1305, 1260, 1190, <sup>d</sup> 1123, 1100, 1080, 1005, 985
(3c)	2.14 (12.4)	4.40 (12.4)	1.76 (12.4)	CH <sub>2</sub> <sup>e</sup> 8.42 CH <sub>2</sub> 8.42 CH <sub>3</sub> 9.16 <sup>f</sup>	1614, 1603, 1554, 1539, 1440, <sup>d</sup> 1427, <sup>d</sup> 1349, <sup>d</sup> 1300, <sup>d</sup> 1260, 1180, <sup>d</sup> 1168, 1130, 1102, 1025, 987
(3d)	2.12 (12.5)	4.38 (12.5)	1.75 (12.5)	C <sub>5</sub> H <sub>10</sub> <sup>d</sup>	1610, 1555, 1538, 1425 1352, 1300, 1270, 1260, 1172, 1158, 1129, 1038, 1000, 985
(3e)	2.12 (12.5)	4.37 (12.5)	1.74 (12.5)	C <sub>4</sub> H <sub>8</sub> <sup>d</sup>	1605, 1557, 1545, 1455, 1435, 1335, 1298, 1270, 1250, 1170, <sup>d</sup> 1110, 1018, 980

<sup>a</sup> In (CD<sub>3</sub>)<sub>2</sub>SO. <sup>b</sup> In Nujol. <sup>c</sup> <sup>1</sup>H n.m.r. in CDCl<sub>3</sub>,  $\tau$  1.76 (1H, d,  $J$  12.3 Hz, H<sub>c</sub>), 4.33 (1H, t,  $J$  12.3 Hz, H<sub>b</sub>), 2.79 (1H, d,  $J$  12.3 Hz, H<sub>a</sub>), 6.60 (4H, q,  $J$  7.2 Hz), and 8.73 (6H, t,  $J$  7.2 Hz, Me). <sup>d</sup> Broad peak. <sup>e</sup> Obscured by solvent. <sup>f</sup>  $J$  7.1 Hz.

(CDCl<sub>3</sub>) 1.69 (1H, d,  $J$  12.3 Hz), 2.87 (1H, d,  $J$  12.3 Hz), 4.28 (1H, t,  $J$  12.3 Hz), 6.59 (4H, q,  $J$  7.2 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 7.73 (3H, s, SMe), and 8.71 (6H, d,  $J$  7.2 Hz, NCH<sub>2</sub>CH<sub>3</sub>),  $\lambda_{\max}$ . (CHCl<sub>3</sub>) 446 nm (log  $\epsilon$  4.625).

**Reaction of the Silver Salt (4) with Picryl Chloride.**—Picryl chloride (0.99 g, 4 mmol) dissolved in *NN*-dimethylformamide (9 ml) was added to (4) (1.25 g, 4 mmol), dissolved in

the same solvent (300 ml). The solution was kept at room temperature for 30 min and then poured into an excess of water. The precipitate was filtered off and crystallized from ethanol to give (*Z,E*)-4-diethylamino-1-nitrobuta-1,3-dienyl picryl sulphide (6), m.p. 144 °C (Found: C, 40.6; H, 3.6; N, 16.9; S, 7.7.  $C_{14}H_{15}N_5O_3S$  requires C, 40.7; H, 3.65; N, 16.95; S, 7.75%),  $\nu_{\max}$ . (Nujol) 1630, 1600, 1560, 1535,

1415, 1340, 1290, 1230—1210, 1170, and 1000  $cm^{-1}$ ,  $\tau$   $[(CD_3)_2CO]$  1.12 (2H, s, ArH), 1.67 (1H, d, *J* 12.3 Hz), 2.12 (1H, d, *J* 12.3 Hz), 4.10 (1H, t, *J* 12.3 Hz), 6.30 (4H, q, *J* 7.2 Hz,  $NCH_2CH_3$ ), and 8.61 (6H, t, *J* 7.2 Hz,  $NCH_2CH_3$ ),  $\lambda_{\max}$ . ( $CHCl_3$ ) 444 nm ( $\log \epsilon$  4.64).

[4/648 Received, 1st April, 1974]

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