

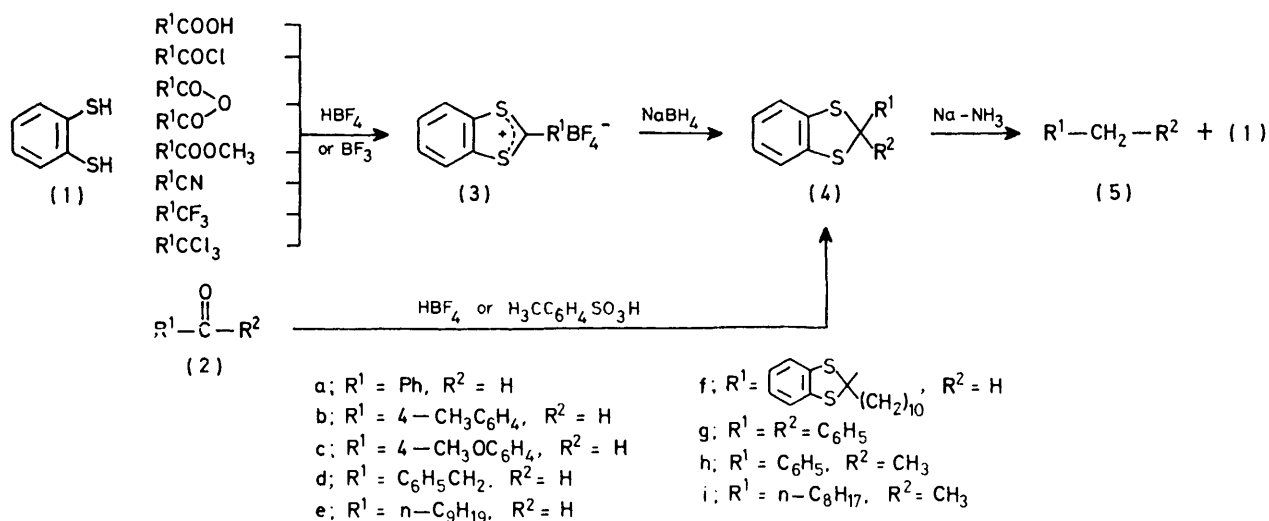
## Pentatomic Heteroaromatic Cations. Part 10.<sup>1</sup> A New Route for the Reduction of the Functional Group of Carboxylic Acids, Acid Chlorides, Anhydrides, Esters, Nitriles, Trihalogenomethyl Compounds, Aldehydes, and Ketones to Methyl or Methylene Groups

By Iacopo Degani and Rita Fochi,\* Istituto di Chimica Organica dell'Università, Via Bidone 36, 10125 Torino, Italy

The reactions of carboxylic acids, acid chlorides, anhydrides, esters, nitriles, and trichloromethyl and trifluoromethyl derivatives with benzene-1,2-dithiol in tetrafluoroboric acid-ether or boron trifluoride-ether, generally affords excellent yields of 2-substituted 1,3-benzodithiolylium tetrafluoroborates. These can be easily reduced with sodium borohydride to 2-substituted 1,3-benzodithiols, which by scission of the C(2)-S bond with sodium in liquid ammonia give the corresponding hydrocarbons. Also the carbonyl group of aldehydes and ketones can be reduced to the methylene group by related reactions.

PREVIOUS work has shown that unsubstituted 1,3-benzodithiolylium salts and their 2-substituted derivatives<sup>2</sup> are remarkably efficient intermediates for the conversion of carboxylic acids, acid chlorides, esters and halides into aldehydes, [*formyl*-<sup>2</sup>H]aldehydes, and ketones.<sup>1,3,4</sup> We now report routes for (a) the rapid preparation of 1,3-benzodithiolylium tetrafluoroborates (3) by reaction of the now readily available benzene-1,2-dithiol<sup>5</sup> with starting compounds with various functional groups; (b) conversion of (3) into hydrocarbons

identical or slightly adapted procedure recently reported for the same reaction with esters.<sup>1</sup> This simple and short procedure, using tetrafluoroboric acid-ether, or exceptionally boron trifluoride-ether, as condensing agent, gives excellent yields of (3) starting from aliphatic and aromatic carboxylic acids, acid chlorides, anhydrides, esters, and aromatic trichloromethyl compounds, and good yields from aromatic nitriles and benzotrifluoride. Unsatisfactory results were obtained from aliphatic nitriles under similar conditions.



by two-step reductive scission of the dithiole ring; and (c) reduction of the carbonyl group of aldehydes and ketones to a methylene group *via* 1,3-benzodithiole derivatives (4).

The preparation of (3) was in all cases performed by an

<sup>1</sup> Part 9, I. Degani and R. Fochi, *Synthesis*, 1977, 263.

<sup>2</sup> For background literature on 1,3-benzodithiolylium, mostly named 1,3-benzodithiolium, salts, see (a) D. S. Breslow and H. Skolnik, in 'Multi-sulfur and Sulfur and Oxygen Five- and Six-membered Heterocycles,' ed. A. Weissberger, Interscience, New York, 1966, ch. 5 and references therein; (b) H. Prinzbach and E. Futterer, *Adv. Heterocyclic Chem.*, 1966, 7, 39 and references therein; (c) E. Campaigne and R. D. Hamilton, *Quart. Reports Sulfur Chem.*, 1970, 5, 275 and references therein; (d) R. Wiziniger, *ibid.*, p. 191 and references therein.

The first step for reducing tetrafluoroborates (3), with sodium borohydride, was carried out mostly on the crude isolated products (procedure A) or sometimes directly on the reaction mixtures (procedure B) and afforded almost quantitative yields of pure 1,3-benzodithiols (4).

The second reduction step was accomplished with sodium in liquid ammonia (in some instances ethyl ether or tetrahydrofuran was added as co-solvent) at reflux temperature. This proved to be a highly selective

<sup>3</sup> I. Degani and R. Fochi, *J.C.S. Perkin I*, 1976, 1886.

<sup>4</sup> I. Degani and R. Fochi, *Synthesis*, 1976, 759.

<sup>5</sup> I. Degani and R. Fochi, *Synthesis*, 1976, 471.

reaction, involving reductive fission of C(2)-S bond <sup>6</sup> by solvated electrons to give generally good yields of hydrocarbons (5). An advantageous feature, amongst others, is the possibility of recovering a large amount of the starting benzene-1,2-dithiol (1).

A reaction closely related to the above is the reduction of aldehydes and ketones to hydrocarbons (5) *via* 1,3-benzodithioles (4). Because of the high overall yields, this procedure provides a useful alternative pathway to other classical methods for converting the carbonyl into methylene group. Furthermore, since it has been shown that 1,3-benzodithioles (4) can be obtained by reaction of unsubstituted or 2-substituted 1,3-benzodithiolium salts with Grignard reagents,<sup>3</sup> it should be pointed out that the hydrogenolysis of (4) represents a new method for hydrocarbon synthesis from halides. Finally, it should be noted that 1,3-benzodithioles, obtained from various classes of compounds, may also be converted into carbonyl derivatives,<sup>2,3</sup> thus increasing the synthetic value of 1,3-benzodithiolium salts.

TABLE 1

Experimental conditions for the preparation of 2-substituted 1,3-benzodithiolium tetrafluoroborates (3a-f) and 1,3-benzodithioles (4a-f)

Starting material (2)	Condensing agent (ml) <sup>a</sup>	t/min <sup>b</sup>
R <sup>1</sup> COOH <sup>c,d</sup>	BF <sub>3</sub> (25)	10
R <sup>1</sup> COCl	BF <sub>3</sub> (25)	5-10
(R <sup>1</sup> CO) <sub>2</sub> O <sup>e,f</sup>	BF <sub>3</sub> (50)	10
R <sup>1</sup> COOCH <sub>3</sub> <sup>d</sup>	BF <sub>3</sub> (50)	10
R <sup>1</sup> CN	BF <sub>3</sub> (50)	30
R <sup>1</sup> CF <sub>3</sub>	1 : 1 BF <sub>3</sub> -CF <sub>3</sub> COOH (50)	30
R <sup>1</sup> CCl <sub>3</sub>	BF <sub>3</sub> (25)	5 <sup>g</sup>
	BF <sub>3</sub> (25)	5 <sup>g</sup>

<sup>a</sup> Referred to 0.05 mol of starting material. <sup>b</sup> At 105-110°.

<sup>c</sup> Starting from HOOC[CH<sub>2</sub>]<sub>10</sub>COOH (0.05 mol), benzene-1,2-dithiol (0.1 mol) and tetrafluoroboric acid (50 ml) was used.

<sup>d</sup> For the reduction of (3d), the salt was dissolved in acetonitrile (150 ml) containing tetrafluoroboric acid (1 ml). <sup>e</sup> Starting from anhydride (0.05 mol), tetrafluoroborate (3) or 1,3-benzodithiole (4) (0.1 mol) was obtained; when instead stoichiometric benzene-1,2-dithiol was used, only 0.05 mol of (3) and (4) was obtained. <sup>f</sup> The amount of sodium borohydride used in procedure A was 5 g, and procedure B 10 g. <sup>g</sup> The trichloromethyl derivative was slowly added to a mixture of (1) and tetrafluoroboric acid or boron trifluoride, with cooling and stirring. The mixture was then maintained for 5 min at room temperature.

## EXPERIMENTAL

*Preparation of 2-Substituted 1,3-Benzodithioles (4) from Carboxylic Acids, Acid Chlorides, Anhydrides, Esters, Nitriles, and Trichloromethyl and Trifluoromethyl Derivatives. General Procedures.*—A. 1,3-Benzodithiolium tetrafluoroborates (3a-f). According to the general procedure previously employed for the preparation of (3) from methyl or phenyl esters,<sup>1</sup> a mixture of the appropriate starting material (2) (0.05 mol) and benzene-1,2-dithiol <sup>5</sup> (1) [(7.1 g, 0.05 mol) when (2) is a carboxylic acid, acid chloride, ester, nitrile, trichloromethyl, or trifluoromethyl derivative; (14.2 g, 0.1 mol) when (2) is an anhydride] in tetrafluoro-

boric acid-ether (54% in ether) or boron trifluoride-ether (45% in ether) was heated at 105-110° in an oil-bath. Details are reported in Table 1. The tetrafluoroborates (3) were precipitated from the cooled mixture by addition of dry ether (150-170 ml), collected by filtration, and washed several times with dry ether. The crude salts were >95% pure (by u.v. analysis) and were used directly in the next stage. The structures were confirmed by comparison of m.p.s and u.v. and n.m.r. spectra with those of authentic samples.<sup>1</sup> Yields and physical data are reported in Table 2.

1,3-Benzodithioles (4a-f). The crude tetrafluoroborates (3) were dissolved in dry acetonitrile (150-250 ml); powdered sodium borohydride (2.5 g) was gradually added, over 10 min, with stirring and cooling in an ice-bath, to the yellow solution which became orange, red, yellow, and then colourless (*ca.* 10-15 min). The mixture was then poured into 5% ammonium chloride solution and extracted with ether. The ether extracts were washed with 5% sodium hydroxide solution and water, dried, and evaporated to yield 1,3-benzodithioles (4).

B. 1,3-Benzodithioles (4d-f). A mixture of the appropriate starting material (2) (0.05 mol) and benzene-1,2-dithiol (1) (0.05 mol or 0.1 mol; see procedure A) in tetrafluoroboric acid was heated at 105-110° as above (for reaction times, see Table 1). After cooling, the mixture was diluted with acetonitrile (150-250 ml) and reduced gradually with sodium borohydride (5 g), as described above, with cooling and stirring until the yellow solution became colourless (*ca.* 20-30 min). The usual work-up gave (4).

Crude 1,3-benzodithioles (4) were sufficiently pure (n.m.r. and t.l.c.) to be used directly in the next stage. Yields and physical data are reported in Table 2.

*Preparation of 2-Substituted 1,3-Benzodithioles (4) from Aldehydes and Ketones. General Procedure.*—Compound (4b) was prepared by reaction at 50-60° for 15 min of a mixture of benzene-1,2-dithiol (1) (7.81 g, 0.055 mol), *p*-toluylaldehyde (6 g, 0.05 mol) and tetrafluoroboric acid-ether (5 ml) in dry benzene (250 ml), according to the general procedure previously reported.<sup>4</sup> In the same way (4d) was prepared from commercial phenylacetaldehyde (50% in benzyl alcohol). The mixture of 2-benzyl-1,3-benzodithiole and benzyl alcohol was chromatographed on silica gel using light petroleum as eluant to afford pure (4d). Compounds (4g-i) were prepared by heating at reflux, in a flask equipped with a water separator, a mixture of benzene-1,2-dithiol (1) (7.81 g, 0.055 mol), the appropriate ketone (0.05 mol), and toluene-*p*-sulphonic acid monohydrate (9.51 g, 0.05 mol) in dry benzene (250 ml) until the starting ketone disappeared [4 and 1 h for (4g and h) respectively by t.l.c.; 30 min for (4i), by i.r.]. The mixture was then poured into water, the benzene layer separated, and the aqueous solution extracted with benzene. The collected benzene layers were washed with 5% sodium hydroxide solution and then water, dried, and evaporated to afford pure (4). Yields and physical data are reported in Table 2.

*Reduction of 2-Substituted 1,3-Benzodithioles (4a-i) to (5) with Sodium in Liquid Ammonia. General Procedure.*—Crude 1,3-benzodithiole (4) (0.05 mol), very finely powdered, was dispersed in liquid ammonia (350-400 ml) with vigorous stirring. When (4) was an oil [(4e and i)] the dispersion was obtained by adding it in solution in ethyl

<sup>6</sup> For an extensive survey of the reductive scission of carbon-sulphur bonds by metal-ammonia solutions and related reagents, see J. L. Wardell, in 'The Chemistry of the Thiol Group,' ed. S. Patai, Interscience, New York, 1974, ch. 4.

<sup>7</sup> P. Appriou and R. Guglielmetti, *Bull. Soc. chim. France*, 1974, 510.

ether (80–100 ml). A solution in tetrahydrofuran (100–120 ml) was used in the cases of (4f and g). Sodium (0.15–0.20 g atom) was added in small pieces; the suspension was

continuous boiling of ammonia. A blue colour which persisted for almost 10 min indicated completion of the reaction. The solvent was then left to evaporate. 10%

TABLE 2

1,3-Benzodithioliylum tetrafluoroborates (3a–f) and 1,3-benzodithioles (4a–i) from carboxylic acids, acid chlorides, anhydrides, esters, nitriles, trihalogenomethyl derivatives, aldehydes, and ketones (2)

Starting material (2)	Procedure	Compound (3)	Yield (%) (2) → (3)	M.p. (°C) <sup>a</sup> (lit. m.p.)	Compound (4)	Yield (%) (2) → (4)	M.p. (°C) <sup>e</sup> or B.p. (°C)/Torr (lit.)
C <sub>6</sub> H <sub>5</sub> COOH	A	(3a)	92	187–188 (187–188) <sup>1</sup>	(4a)	87	72–73 (72–73) <sup>3</sup>
4-H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> COOH	A	(3b)	96	167–168 (167–168) <sup>1</sup>	(4b)	90	77–78 <sup>d</sup>
4-H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> COOH	A	(3c)	97	263–264 (263–264) <sup>1</sup>	(4c)	90	71–72 (71–72) <sup>3</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COOH	A	(3d)	95	94–96 <sup>e</sup>	(4d)	93	53–54 <sup>f</sup> (51–53) <sup>8</sup>
n-C <sub>9</sub> H <sub>19</sub> COOH	A	(3e) <sup>g</sup>			(4d)	91	53–54
	B				(4e)	85	164–165/0.2 (164–165/0.2) <sup>4</sup>
HOOC[CH <sub>2</sub> ] <sub>10</sub> COOH	A	(3f)	99	106–108 <sup>h</sup>	(4e)	94	164–165/0.2
	B				(4f)	98	71–72 <sup>i,j</sup>
C <sub>6</sub> H <sub>5</sub> COCl	A	(3a)	100	187–188	(4a)	97	71–72
4-H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> COCl	A	(3b)	97	167–168	(4b)	96	72–73
4-H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> COCl	A	(3c)	100	263–264	(4c)	97	71–72
n-C <sub>9</sub> H <sub>19</sub> COCl	B				(4e)	100	164–165/0.2
(C <sub>6</sub> H <sub>5</sub> CO) <sub>2</sub> O	A	(3a)	97	187–188	(4a)	93	72–73
(4-H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> CO) <sub>2</sub> O	A	(3b)	98	167–168	(4b)	96	77–78
(4-H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> CO) <sub>2</sub> O	A	(3c)	98	263–264	(4c)	98	71–72
(n-C <sub>9</sub> H <sub>19</sub> CO) <sub>2</sub> O	B				(4e)	93	164–165/0.2
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COOCH <sub>3</sub>	A	(3d)	90	94–96	(4d)	86	53–54
	B				(4d)	87	53–54
n-C <sub>9</sub> H <sub>19</sub> COOCH <sub>3</sub>	B				(4e)	93	164–165/0.2
C <sub>6</sub> H <sub>5</sub> CN	A	<i>k</i>			(4a)	62	72–73
4-H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> CN	A	<i>k</i>			(4b)	58	77–78
C <sub>6</sub> H <sub>5</sub> CF <sub>3</sub>	A	(3a)	60	187–188	(4a)	57	72–73
C <sub>6</sub> H <sub>5</sub> CCl <sub>3</sub>	A	(3a)	100	187–188	(4a)	100	72–73
4-H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> CCl <sub>3</sub>	A	(3c)	95	263–264	(4c)	94	71–72
4-H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> CHO					(4b)	97	77–78
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CHO					(4d)	98	53–54
C <sub>6</sub> H <sub>5</sub> COC <sub>6</sub> H <sub>5</sub>					(4g)	100	122–123 (122–123) <sup>3</sup>
C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>					(4h)	100	82–83 (82–83) <sup>3</sup>
n-C <sub>8</sub> H <sub>17</sub> COCH <sub>3</sub>					(4i)	98	160–161/3 <sup>i</sup>

<sup>a</sup> Recrystallized from acetonitrile–ether and a few drops of tetrafluoroboric acid; melting was always preceded by decomposition, the data reported refer to the temperature at which final melting took place. U.v. spectra in H<sub>2</sub>SO<sub>4</sub> were identical to those previously reported.<sup>1</sup> <sup>b</sup> Overall yields from the starting material. <sup>c</sup> Recrystallized from 95% ethanol, unless otherwise noted. <sup>d</sup> Found: C, 68.95; H, 5.0; S, 26.1. C<sub>14</sub>H<sub>12</sub>S<sub>2</sub> requires C, 68.8; H, 4.95; S, 26.25%;  $\delta$  (CDCl<sub>3</sub>) 2.22 (s, CH<sub>3</sub>), 6.18 (s, CH), and 6.90–7.52 (8 H, m, aromatic). <sup>e</sup> Found: C, 50.8; H, 3.3; S, 19.6. C<sub>14</sub>H<sub>11</sub>BF<sub>4</sub>S<sub>2</sub> requires C, 50.95; H, 3.35; S, 19.4%;  $\delta$  (CF<sub>3</sub>-COOD) 5.12 (s, CH<sub>2</sub>), 7.52 (s, C<sub>6</sub>H<sub>5</sub>), 7.95–8.15 (m, H-5 and -6), and 8.50–8.70 (m, H-4 and -7), identical with that reported for the corresponding perchlorate;<sup>7</sup> u.v. spectrum of the solution prepared by dissolving (3d) in acetonitrile (1 ml) containing 2% H<sub>2</sub>SO<sub>4</sub> (96%) and then diluted with H<sub>2</sub>SO<sub>4</sub> (96%) under cooling,  $\lambda_{\max}$  253 nm (log  $\epsilon$  3.74), 257sh (3.83), 258 (3.85), 262 (3.86), and 320 nm (3.79). <sup>f</sup>  $\delta$  (CDCl<sub>3</sub>) 3.21 (d, CH, *J* 7.5 Hz), 5.05 (5, CH<sub>2</sub>, *J* 7.5 Hz), and 6.98–7.42 (9 H, m, aromatic). <sup>g</sup> Did not solidify as the corresponding perchlorate.<sup>4</sup> The separation of the salt was modified as follows: after addition of dry ether, the mixture was left in a refrigerator for 10–15 min, after which the ether solution was easily decanted. The oily residue was then reduced as described in procedure A. <sup>h</sup> Recrystallized from benzene–acetonitrile (1 : 1)–ether and a few drops of tetrafluoroboric acid (Found: C, 46.5; H, 4.4; S, 20.6. C<sub>24</sub>H<sub>28</sub>B<sub>3</sub>F<sub>8</sub>S<sub>4</sub> requires C, 46.6; H, 4.55; S, 20.75%);  $\delta$  (CF<sub>3</sub>COOD) 1.15–2.45 (m, CH<sub>2</sub>), 3.93 (t, and CH<sub>2</sub>, *J* 7.5 Hz), 8.08–8.35 (m, H-5 and -6), and 8.60–8.90 (m, H-4 and -7); u.v. spectrum of the solution prepared as described in note *e*,  $\lambda_{\max}$  253 (log  $\epsilon$  4.02), 257sh (4.15), 258 (4.16), 262 (4.19), 314 (4.20), and 335 sh nm (3.98). <sup>i</sup> Recrystallized from benzene–ethanol. <sup>j</sup> Found: C, 64.45; H, 6.7; S, 28.6. C<sub>24</sub>H<sub>30</sub>S<sub>4</sub> requires C, 64.5; H, 6.75; S, 28.7%;  $\delta$  (CDCl<sub>3</sub>) 1.15–2.13 (m, 10 CH<sub>2</sub>), 4.85 (t, 2 CH, *J* 7.2 Hz), and 6.92–7.35 (8 H, m, aromatic). <sup>k</sup> Ammonium tetrafluoroborate precipitated during the reaction. The following step was performed on the mixture of salt (3) and ammonium tetrafluoroborate according to procedure A. However pure salt (3) could be obtained by treating the mixture with acetonitrile (*ca.* 10–15 ml); insoluble ammonium tetrafluoroborate was filtered off and salt (3) was reprecipitated by addition of dry ether. <sup>l</sup> (Found: C, 68.55; H, 8.65; S, 22.65. C<sub>16</sub>H<sub>14</sub>S<sub>2</sub> requires C, 68.5; H, 8.6; S, 22.85%);  $\delta$  (CDCl<sub>3</sub>) 0.72–2.20 (m, C<sub>8</sub>H<sub>17</sub>), 1.79 (s, CH<sub>3</sub>), and 6.88–7.32 (4 H, m, aromatic).

allowed to decolorize before each successive piece was added. During addition (*ca.* 30 min), an ethanol bath was occasionally placed under the reaction flask to ensure

Ammonium chloride solution (100 ml) containing crushed ice (*ca.* 100 g) was added to the solid residue and the mixture was extracted with ether. The alkaline solution was acidified with hydrochloric acid; the residue obtained by the usual work-up with ether extraction was distilled

<sup>8</sup> H. A. Staab and B. Draeger, *Chem. Ber.*, 1972, **105**, 2320.

under reduced pressure to afford pure benzene-1,2-dithiol (see Table 3). The ether extracts were washed with 5% 30) showed only (5) and solvent] which was carefully fractionated to give pure (5). Compounds (5) were

TABLE 3  
Yields of (5) and (1) by reduction of (4) with sodium and ammonia

Reduction product (5)	1,3-Benzodithiole (4)	Yield <sup>a</sup> (%)	B.p. (°C)/ Torr	Lit., <sup>9</sup> b.p. (°C)/ Torr	Yield <sup>b</sup> (%) of (1)
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	(4a)	50 <sup>c</sup>			70
4-H <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	(4b)	76	137—138/760	137.5—138/760	75
4-H <sub>3</sub> COC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	(4c)	84	174—175/760	175—176/760	78
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>3</sub>	(4d)	74	135/760	135.5/760	79
	(4h)	76	135/760		82
n-C <sub>10</sub> H <sub>22</sub>	(4e)	93	173/760	174/760	88
	(4i)	89	173/760		88
n-C <sub>12</sub> H <sub>26</sub>	(4f) <sup>d</sup>	82	91/12	98/15	70
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	(4g) <sup>e</sup>	67	141—142/22	158/35	63

<sup>a</sup> Yield of pure distilled product starting from the crude 1,3-benzodithiole (4). <sup>b</sup> Yield of pure distilled product, which solidified spontaneously, b.p. 114—115° at 14 Torr, m.p. 27—28° (lit.,<sup>5</sup> b.p. 110—111° at 12 Torr, m.p. 27—28°). <sup>c</sup> Yield by g.l.c. During evaporation of ammonia, no particular device was adopted for fully trapping toluene. <sup>d</sup> 0.4 g atom of sodium were used for 0.05 mol of (4f). <sup>e</sup> A mixture of diphenylmethane and benzophenone (2 : 1 by g.l.c.) was obtained when the reaction was carried out in the absence of tetrahydrofuran.

sodium hydroxide solution and then water, dried, and concentrated to give a clear oil [g.l.c. (SE 30, 5% over Varaport

<sup>9</sup> I. Heilbronn, in 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

identified by comparison of their b.p., i.r., and n.m.r. data, and g.l.c. retention times with those of authentic samples. Details are listed in Table 3.

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