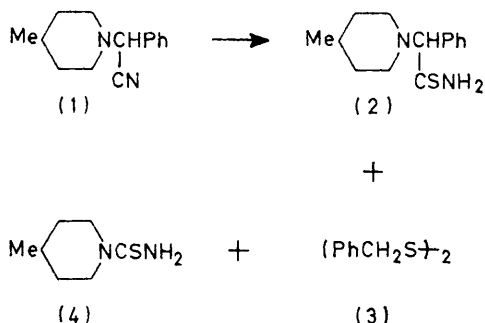


## A Novel Synthesis of Thiols from $\alpha$ -Amino-nitriles

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Reaction of  $\alpha$ -alkylamino-nitriles [ $R^1R^2C(NHR^3)CN$ ] with hydrogen sulphide under mild conditions gives high yields of thiols ( $R^1R^2CHSH$ ) with none of the anticipated  $\alpha$ -amino-thioamides. Under the same conditions the parent aldehydes, thioaldehydes, and corresponding imines give only mixtures of polysulphides.

PREPARATION of thioamides by the action of hydrogen sulphide on nitriles in the presence of pyridine and triethylamine is well documented.<sup>1</sup> In contrast, reaction of  $\alpha$ -amino-nitriles with hydrogen sulphide has



received little attention and the few reports are concerned mostly with  $\alpha$ -(tertiary amino)-nitriles which give the expected  $\alpha$ -(tertiary amino)-thioamides.<sup>2</sup> A notable

and  $\alpha$ -anilinoacetonitrile have both been treated<sup>4</sup> with hydrogen sulphide to give the corresponding thioamide.

We have now found that  $\alpha$ -(secondary amino)-nitriles [ $R^1R^2C(NHR^3)CN$ ] react with hydrogen sulphide at room temperature to give thiols ( $R^1R^2CHSH$ ) in a novel, high yield conversion of aldehydes and ketones into thiols.

Of the many routes to primary, secondary, and tertiary  $\alpha$ -amino-nitriles from aldehydes and ketones, the general method of Hauser<sup>5</sup> was the most satisfactory. The aminonitriles used in this study are summarised in Table 1 and their properties given in Table 3 (see Experimental section).

The  $\alpha$ -amino-nitriles were treated with hydrogen sulphide under standard conditions (unless otherwise stated) and Table 1 summarises the products obtained. The reaction was most successful with the  $\alpha$ -isopropylamino- and  $\alpha$ -t-butylamino-nitriles derived from either aldehydes or ketones, giving high yields of thiols, but

TABLE 1<sup>a</sup>  
Reaction of  $\alpha$ -amino-nitriles with hydrogen sulphide

$\alpha$ -Amino-nitrile $R^1R^2C(NR^3R^4)CN$	$R^1$	$R^2$	$R^3$	$R^4$	Yield (%)	
					$R^1R^2CHSH$	$(R^1R^2CHS)_2$
(5) <sup>b</sup>	3,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	Pr <sup>i</sup>	92	0
(6)	4-(MeO)C <sub>6</sub> H <sub>4</sub>	H	H	Pr <sup>i</sup>	0	80 <sup>c,d</sup>
(7) <sup>e</sup>	3,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	Bu <sup>t</sup>	80 <sup>e</sup>	0
(8)	Ph	Me	H	Pr <sup>i</sup>	96	0
(9)	Ph	H	H	Pr <sup>i</sup>	56 <sup>f</sup>	0
(10) <sup>b</sup>	3,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	Me	0	80 <sup>d,g</sup>
(11)	[CH <sub>2</sub> ] <sub>5</sub>	H	H	Pr <sup>i</sup>	8 <sup>o,h</sup>	0
(12) <sup>b</sup>	3,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	Me	Me	0 <sup>e,i</sup>	0
(13) <sup>e</sup>	Ph	H	Me	Me	0 <sup>e,j</sup>	0
(14)	3,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	H	Ph	0 <sup>k</sup>	0
(15) <sup>l</sup>	Ph	H	H	H	0 <sup>m</sup>	0

<sup>a</sup> See Experimental section for physical properties of products. <sup>b</sup> J. Klosa, *J. prakt. Chem.*, 1961, **12**, 258. <sup>c</sup> Balance recovered as unchanged amino-nitrile. <sup>d</sup> The thiol was obtained initially but was oxidised rapidly in air (see N. Kharasch, 'Organic Sulphur Compounds,' Pergamon Press, London, 1961, vol. I, p. 97). <sup>e</sup> Ref. 5. <sup>f</sup>  $\alpha$ -Isopropylamino-( $\alpha$ -phenyl)thioacetamide (37%) was also isolated. <sup>g</sup>  $\alpha$ -(3,4-Dimethoxyphenyl)-( $\alpha$ -methylamino)thioacetamide (20%) was also isolated. <sup>h</sup> Extended reaction time (3 days) gave cyclohexanethiol (35%). <sup>i</sup>  $\alpha$ -(3,4-Dimethoxyphenyl)-( $\alpha$ -dimethylamino)thioacetamide (25%) was isolated. <sup>j</sup>  $\alpha$ -Dimethylamino-( $\alpha$ -phenyl)thioacetamide (25%) was isolated. <sup>k</sup>  $\alpha$ -Anilino- $\alpha$ -(3,4-dimethoxyphenyl)thioacetamide (90%) was isolated. <sup>l</sup> Ref. 4. <sup>m</sup>  $\alpha$ -Amino-( $\alpha$ -phenyl)thioacetamide (95%) was isolated.

exception<sup>3</sup> is  $\alpha$ -(4-methylpiperidino)- $\alpha$ -phenylacetone nitrile (1) which gives a mixture of the thioamide (2) (8%), the disulphide (3) (9%), and the thiourea (4) (34%) when heated in a sealed tube at 180 °C for 7 h with a solution of ethanol saturated with ammonia and hydrogen sulphide.  $\alpha$ -Amino- $\alpha$ -phenylacetone nitrile

<sup>1</sup> (a) K. A. Petrov and L. N. Andreev, *Russ. Chem. Rev.*, 1969, **38**, 21; (b) T. S. Gardner, E. Wenir, and J. Lee, *J. Org. Chem.*, 1954, **19**, 753; (c) P. A. Janssen, D. Zivkovic and P. Demoen, *J. Amer. Pharm. Assoc. (Sci. Edn.)*, 1955, **44**, 465; (d) X. Pascaud and M. Lambie, *Arzneim-Forsch.*, 1971, **10**, 1547.

<sup>2</sup> (a) R. A. Henry and W. M. Dehn, *J. Amer. Chem. Soc.*, 1950, **72**, 2804; (b) R. Turner and C. Djerassi, *ibid.*, p. 3081.

was unsuccessful with all the primary and tertiary amino-nitriles studied, giving only the normal thioamide products.

In the absence of pyridine and triethylamine,  $\alpha$ -(3,4-dimethoxyphenyl)- $\alpha$ -isopropylaminoacetonitrile (5) reacted quantitatively with hydrogen sulphide to give

<sup>3</sup> H. Najer, P. Chabrier, R. Guidicelli, and J. Sette, *Bull. Soc. chim. France*, 1958, 1189.

<sup>4</sup> (a) A. H. Cook, I. Heilbron, and A. P. Mahadevan, *J. Chem. Soc.*, 1941, 1061; (b) A. E. Fairfull, J. L. Lowe, and D. A. Peak, *ibid.*, 1951, 742.

<sup>5</sup> C. R. Hauser and G. F. Morris, *J. Org. Chem.*, 1961, **26**, 4741.

dimeric 3,4-dimethoxythioveratraldehyde (thioveratraldehyde) which was characterised by elemental analysis, molecular weight, and by comparison of its i.r. and n.m.r. spectra with those of monomeric thioveratraldehyde independently synthesised by treating veratraldehyde with hydrogen sulphide in the presence of hydrogen chloride. Further reaction of the dimeric thioveratraldehyde with hydrogen sulphide, under the standard conditions, gave a mixture of bis-(3,4-dimethoxybenzyl) disulphide and polysulphides. The former component was identified by g.l.c. and n.m.r. comparison with authentic material and the latter by n.m.r. The ratio of disulphide to polysulphides in the mixture was determined by n.m.r. analysis of the  $\alpha$ -CH<sub>2</sub> protons in the disulphide ( $\delta$  3.56) and in the polysulphides [ $\delta$  3.96, 4.08, and 4.12 (3 singlets)]. An identical mixture of disulphide and polysulphides was obtained directly from veratraldehyde on reaction with hydrogen sulphide under the standard conditions, establishing that neither the aldehyde nor the thioaldehyde participate in the conversion of amino-nitriles into thiols.

Since imines are readily available from  $\alpha$ -amino-nitriles,<sup>6</sup> their reaction with hydrogen sulphide under the standard conditions was investigated (a) as a possible alternative source of thiols and (b) to establish if they participate in the conversion of amino-nitriles to thiols. Table 4 (Experimental section) summarises the properties of the imines used in this study and Table 2

TABLE 2

Reactions of  $\alpha$ -amino-nitriles and of imines 3,4-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CH·NX with hydrogen sulphide

$\alpha$ -Amino-nitrile	Imine	X	Yields (%) *			
			Thioamide	Thiol	Disulphide	Polysulphides
(5)	(16)	Pr <sup>l</sup>	0 (0)	92 (0)	0 (40)	0 (60)
(7)	(17)	Bu <sup>t</sup>	0 (0)	90 (0)	0 (40)	0 (60)
(10)	(18)	Me	20 (0)	0 (10)	80 (44)	0 (56)
(14)	(19)	Ph	90 (0)	0 (0)	0 (20)	0 (80)

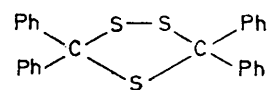
\* Figures in parentheses refer to yields obtained from imines.

shows a comparison of the products obtained when the amino-nitriles (5), (7), (10), and (14) and the corresponding imines (16)–(19) were treated with hydrogen sulphide. The disulphide and polysulphides obtained from the imines were identical with those obtained from veratraldehyde and thioveratraldehyde under the same conditions and the ratio of disulphide to polysulphides was similarly determined by n.m.r. analysis. 3,4-Dimethoxytoluene- $\alpha$ -dithiol would appear to be a common intermediate in these reactions since *gem*-dithiols have been reported<sup>7</sup> (a) as intermediates in the reaction of imines with hydrogen sulphide and in the conversion of aldehydes into thioaldehydes and (b) to

<sup>6</sup> (a) E. W. Drew and P. D. Ritchie, *Chem. and Ind.*, 1952, 1104; (b) T. Delphine, *Bull. Soc. chim. France*, 1903, 29, 1190.

<sup>7</sup> (a) B. Magnusson, *Acta Chem. Scand.*, 1962, 16, 1536; (b) T. Cairns, G. Evans, A. Larcher, and B. McKuswick, *J. Amer. Chem. Soc.*, 1952, 74, 3982; (c) R. Mayer, *Angew. Chem. Internat. Edn.*, 1963, 2, 370; (d) N. Kharasch, 'Organic Sulphur Compounds,' vol. 1 Pergamon Press, London, 1961, pp. 134, 140, 141.

react further with hydrogen sulphide to give polysulphides. The formation of polysulphides from imines but not from amino-nitriles demonstrates that imines are unlikely to participate in the conversion of amino-nitriles into thiols.



(20)

The thio-ozonide (20) has recently been isolated<sup>8</sup> in low yield from the nucleophilic addition of amines to thiobenzophenone, and to support a *gem*-thiolamine intermediate *N*-phenyldiphenylmethanimine was treated with hydrogen sulphide under neutral conditions to give a mixture of the thio-ozonide (20) and thiobenzophenone. Since no thio-ozonides nor thioaldehydes were detected by n.m.r. analysis of the products from the reaction of the imines (16)–(19) with hydrogen sulphide under basic conditions, a *gem*-dithiol intermediate would appear to be more likely than the corresponding *gem*-thiolamine.

## EXPERIMENTAL

M.p.s were determined with a Mettler FPI instrument, microanalyses with a Perkin-Elmer model 240 machine, and molecular weights were determined by the Rast method. N.m.r. spectra were measured at 100 MHz with a Varian HA100 spectrometer for solutions in deuteriochloroform with tetramethylsilane as internal standard. G.l.c. was performed on a Perkin-Elmer F11 instrument with a 15% C20M column at 200 °C unless otherwise stated.

*Preparation of  $\alpha$ -Amino-nitriles.*—A solution of the aldehyde (0.2 mol) and sodium metabisulphite (0.1 mol) in water (200 ml) was treated with a 25% aqueous solution of the amine (36 ml) at room temperature. After 10 min the mixture was treated with sodium cyanide (0.2 mol) and after 2.5 h at room temperature was extracted with ether (2 × 100 ml). The combined extracts were washed with 2N-HCl (2 × 50 ml), and the combined washings were adjusted to pH 10.0 with sodium carbonate and extracted with ether (3 × 50 ml). The combined ethereal extracts were dried (MgSO<sub>4</sub>) and the solvent was removed *in vacuo* to afford the required amino-nitrile; the physical data are listed in Table 3.

*Reaction of  $\alpha$ -Amino-nitriles with Hydrogen Sulphide.*—A solution of the  $\alpha$ -amino-nitrile (5 g) in anhydrous pyridine (20 ml) and triethylamine (6 ml) was treated with a slow stream of H<sub>2</sub>S gas at room temperature for 2 h during which time the mixture became warm (35°) and the colour changed to red or green. The reaction flask was sealed and kept at room temperature for 16 h. The volatile materials were removed *in vacuo* and the residual oil dissolved in ether (100 ml), washed with water (3 × 20 ml), 2N-HCl (2 × 50 ml), and water (2 × 50 ml). The acid washings were retained and the ethereal solution was dried (MgSO<sub>4</sub>) and evaporated *in vacuo* to give the thiol, which was characterised as the 2,4-dinitrophenyl thioether,<sup>9</sup> the

<sup>8</sup> M. M. Cambell and D. M. Evgenios, *J.C.S. Perkin I*, 1973, 2862.

<sup>9</sup> A. Vogel, 'Practical Organic Chemistry,' 3rd edn., Longmans, Green and Co., London, 1956, p. 500.

mercury(II) chloride complex,<sup>10</sup> or as the crystalline disulphide, obtained by oxidation in air.

The combined acid washings were adjusted to pH 9.0 with sodium carbonate and extracted with ether (3 × 50 ml) and the combined extracts were washed with brine (2 × 50 ml), dried (MgSO<sub>4</sub>), and evaporated *in vacuo* to yield either recovered  $\alpha$ -aminonitrile or the crystalline  $\alpha$ -amino-thioamide.

The following  $\alpha$ -amino-nitriles were treated with hydrogen sulphide by this procedure to give the products shown.

(i)  $\alpha$ -(3,4-Dimethoxyphenyl)- $\alpha$ -isopropylaminoacetonitrile (5). Product: 3,4-dimethoxytoluene- $\alpha$ -thiol<sup>11</sup> (92%); g.l.c. (10% XE 60, 200 °C)  $R_t$  5.5 min;  $\delta$  1.70 (1H, t,

Calc. for C<sub>18</sub>H<sub>22</sub>S<sub>2</sub>: C, 59.9; H, 6.0%),  $\delta$  3.56 (4H, s,  $\alpha$ -CH<sub>2</sub>), 3.81 (6H, s, OCH<sub>3</sub>), 3.83 (6H, s, OCH<sub>3</sub>), and 6.76 (6H, s, aromatic H).

(vii) 2-Isopropylaminocyclohexanecarbonitrile (11). Product: cyclohexanethiol (8%, and after 3 days under standard conditions 35%). The 2,4-dinitrophenyl thioether was prepared and isolated as pale yellow needles, m.p. 148° (lit.,<sup>9</sup> 148°).

(viii)  $\alpha$ -(3,4-Dimethoxyphenyl)- $\alpha$ -dimethylaminoacetonitrile (12). Product:  $\alpha$ -(3,4-dimethoxyphenyl)-( $\alpha$ -dimethylamino)-thioacetamide (25%), m.p. 176° (needles from ethyl acetate) (Found: C, 57.0; H, 7.2; N, 10.9. C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 56.6; H, 7.1; N, 11.0%).

TABLE 3  
 $\alpha$ -Amino-nitriles

Compound	Yield (%)	M.p. (°C)	Analysis						
			Found (%)			Formula	Required (%)		
			C	H	N			C	H
(5)	79	102	67.0	7.9	12.2	C <sub>18</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	66.6	7.7	11.9
(6) <sup>a</sup>	73	123	60.0	7.3	11.3	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O.HCl	59.9	7.1	11.6
(7) <sup>b</sup>	80	69							
(8) <sup>a</sup>	96	109	64.1	7.6	12.2	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> .HCl	64.1	7.6	12.4
(9)	70	<i>c</i>	75.6	8.2	16.1	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub>	75.8	8.1	16.1
(10) <sup>a</sup>	65	152	54.2	6.2	11.0	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> .HCl	54.4	6.2	11.5
(11) <sup>a</sup>	95	132	59.4	9.7	13.8	C <sub>10</sub> H <sub>18</sub> N <sub>2</sub> .HCl	59.2	9.4	13.8
(12) <sup>a</sup>	85	167	56.4	6.8	10.5	C <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> .HCl	56.1	6.7	10.9
(13) <sup>a</sup>	80	182	60.9	6.9	13.9	C <sub>10</sub> H <sub>12</sub> N <sub>2</sub> .HCl	61.0	6.6	14.2
(14)	85	147	63.7	6.0	9.0	C <sub>16</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	63.5	6.1	9.2
(15) <sup>d</sup>	90	55							

<sup>a</sup> Characterised as hydrochloride. <sup>b</sup> Ref. 5. <sup>c</sup> Liquid decomposing on distillation. <sup>d</sup> Ref. 4.

$J$  7.5 Hz, SH), 3.64 (2H, d,  $J$  7.5 Hz,  $\alpha$ -CH<sub>2</sub>), 3.81 (3H, s, OCH<sub>3</sub>), 3.84 (3H, s, OCH<sub>3</sub>), and 6.8 (3H, m, aromatic H). The 2,4-dinitrophenyl thioether gave pale yellow needles (95%), m.p. 159° (Found: C, 51.7; H, 4.1; N, 7.8. C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>6</sub>S requires C, 51.4; H, 4.0; N, 7.9%).

(ii)  $\alpha$ -Isopropylamino- $\alpha$ -(4-methoxyphenyl)acetonitrile (6). Product: bis-(4-methoxybenzyl) disulphide (80%) isolated as needles, m.p. 101°; g.l.c.  $R_t$  54 min (Found: C, 63.0; H, 5.9. C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>S<sub>2</sub> requires C, 62.7; H, 5.9%).

(iii)  $\alpha$ -*t*-Butylamino- $\alpha$ -(3,4-dimethoxyphenyl)acetonitrile (7). Product: 3,4-dimethoxytoluene- $\alpha$ -thiol (80%); g.l.c. (10% XE 60, 200 °C)  $R_t$  5.5 min.

(iv)  $\alpha$ -Isopropylamino- $\alpha$ -phenylpropionitrile (8). Product: 1-phenylethanethiol (96%);<sup>12</sup> g.l.c.  $R_t$  1.5 min. The mercury(II) chloride derivative gave needles, m.p. 72.5° (lit.,<sup>10</sup> 73.5°) (Found: Cl, 8.4; S, 9.5. Calc. for C<sub>8</sub>H<sub>8</sub>ClHgS: Cl, 9.5; S, 8.6%).

(v)  $\alpha$ -Isopropylamino- $\alpha$ -phenylacetonitrile (9). Product (a): toluene- $\alpha$ -thiol (56%); g.l.c.  $R_t$  0.5 min. The 2,4-dinitrophenylthioether gave pale yellow needles, m.p. 130° (lit.,<sup>9</sup> 130°). In the presence of oxygen for 24 h toluene- $\alpha$ -thiol was completely converted into dibenzyl disulphide, m.p. 71° (lit.,<sup>13</sup> 71°); g.l.c.  $R_t$  18 min (Found: C, 68.7; H, 5.9. Calc. for C<sub>14</sub>H<sub>14</sub>S<sub>2</sub>: C, 68.2; H, 5.7%). Product (b):  $\alpha$ -isopropylamino-( $\alpha$ -phenyl)thioacetamide (37%), m.p. 98.6° (Found: C, 63.9; H, 7.9; N, 13.4. C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>S requires C, 63.4; H, 7.7; N, 13.4%).

(vi)  $\alpha$ -(3,4-Dimethoxyphenyl)- $\alpha$ -methylaminoacetonitrile (10). Product (a): bis-(3,4-dimethoxybenzyl) disulphide (80%), m.p. 83° (needles from propan-2-ol) (lit.,<sup>11</sup> 83°); g.l.c. (2% OV1, 240°)  $R_t$  3.5 min (Found: C, 59.3; H, 6.1.

(ix)  $\alpha$ -Dimethylamino- $\alpha$ -phenylacetonitrile (13). Product:  $\alpha$ -dimethylamino-( $\alpha$ -phenyl)thioacetamide (25%), m.p. 147° (needles from di-isopropyl ether) (Found: C, 61.9; H, 7.2; N, 14.2. C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>S requires C, 61.8; H, 7.2; N, 14.4%).

(x)  $\alpha$ -Anilino- $\alpha$ -(3,4-dimethoxyphenyl)acetonitrile (14). Product:  $\alpha$ -anilino- $\alpha$ -(3,4-dimethoxyphenyl)thioacetamide (90%), m.p. 171° (needles from propan-2-ol) (Found: C, 63.7; H, 6.0; N, 9.0. C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S requires C, 63.5; H, 6.0; N, 9.2%).

(xi)  $\alpha$ -Amino- $\alpha$ -phenylacetonitrile (15). Product:  $\alpha$ -amino-( $\alpha$ -phenyl)thioacetamide (95%) characterised as the hydrochloride, m.p. 218° (needles from propan-2-ol) (lit.,<sup>4</sup> 218°) (Found: C, 46.8; H, 5.4; N, 13.3. Calc. for C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>S.HCl: C, 47.4; H, 5.4; N, 13.8%).

*General Procedure for the Preparation of Imines.*—The appropriate amine (0.22 mol) was added dropwise with stirring to veratraldehyde (0.2 mol) at 0 °C. The reaction mixture was stirred for 16 h at room temperature and the resultant solid recrystallised to give the imine (see Table 4).

*Reaction of Imines with Hydrogen Sulphide.*—The imines (16)–(19) were treated with hydrogen sulphide by the standard procedure described for  $\alpha$ -amino-nitriles and in each case work-up for neutral components gave complete conversion into a mixture of bis-(3,4-dimethoxybenzyl) disulphide and bis-(3,4-dimethoxybenzyl) polysulphides; the former was identified by g.l.c. (2% OV1, 240 °C)  $R_t$  3.5 min and n.m.r.,  $\delta$  3.56 (4H, s,  $\alpha$ -CH<sub>2</sub>), 3.81 (6H, s, OCH<sub>3</sub>), 3.83 (6H, s, OCH<sub>3</sub>), and 6.76 (6H, s, aromatic H) and the latter by n.m.r.,  $\delta$  3.81 (s, OCH<sub>3</sub>), 3.96, 4.08, and 4.12 (each s,  $\alpha$ -CH<sub>2</sub>), and 6.8, 6.81, and 6.83 (each s,

<sup>11</sup> L. Nutting, R. Silverstein, and C. Himel, U.S.P. 2,957,919 (Chem. Abs., 1962, 55, 54,266).

<sup>12</sup> J. H. Brewster, *J. Amer. Chem. Soc.*, 1959, 81, 5475.

<sup>13</sup> O. Hinsberg, *Chem. Ber.*, 1912, 45, 2337.

<sup>10</sup> B. Halmberg, *Arkiv. Kemi. Min., Geol.*, 1937, 12A, No. 14, 10 (Chem. Abs., 1937, 31, 4292).

aromatic H). The ratio of products was determined by integration of the n.m.r. absorption of the  $\alpha$ -CH<sub>2</sub> protons as summarised in Table 2.

*Thioveratraldehyde*.—(a) A solution of veratraldehyde (10 g, 0.06 mol) in ethanol (100 ml) was cooled to 0 °C, treated with a slow stream of HCl gas for 2 h, and then with a simultaneous slow stream of H<sub>2</sub>S gas for a further 2 h. The solid was removed, washed with ethanol, and dried to

*Reaction of Dimeric Thioveratraldehyde with Hydrogen Sulphide*.—Under the standard reaction conditions, dimeric thioveratraldehyde was quantitatively converted into a mixture of bis-(3,4-dimethoxybenzyl) disulphide, g.l.c. (2% OV1, 240°) *R<sub>t</sub>* 3.5 min and bis-(3,4-dimethoxybenzyl) polysulphides,  $\delta$  3.56 ( $\alpha$ -CH<sub>2</sub>, disulphide) and 3.96, 4.08, and 4.12 ( $\alpha$ -CH<sub>2</sub>, polysulphides) shown by integration to be in the ratio 2 : 5.

TABLE 4  
Imines

Compound	Yield (%)	M.p. (°C)	Analysis						
			Found (%)			Formula	Required (%)		
			C	H	N		C	H	N
(16)	95	94 <sup>a</sup>	69.6	8.4	6.4	C <sub>12</sub> H <sub>17</sub> NO <sub>2</sub>	69.5	8.3	6.7
(17)	90	73 <sup>b</sup>	70.7	8.6	6.0	C <sub>13</sub> H <sub>19</sub> NO <sub>2</sub>	70.5	8.65	6.3
(18) <sup>c</sup>	98	56 <sup>b</sup>							
(19)	98	86 <sup>b</sup>	74.7	6.4	5.5	C <sub>15</sub> H <sub>15</sub> NO <sub>2</sub>	74.6	6.2	5.8

<sup>a</sup> Recrystallized from propan-2-ol as needles. <sup>b</sup> Recrystallized from petroleum (b.p. 40–60°) as needles. <sup>c</sup> R. Moffatt and W. Hoehn, *J. Amer. Chem. Soc.*, 1947, **69**, 1792.

give the title compound as a pale yellow powder (11 g, 100%), m.p. 220° (Found: C, 59.2; H, 5.6%; *m/e*, 193. C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>S requires C, 59.3; H, 5.5%; *M*, 182),  $\delta$  3.82 (3H, s, OCH<sub>3</sub>), 3.85 (3H, s, OCH<sub>3</sub>), 5.3 (1H, s, CHS), and 6.8–7.1 (3H, m, aromatic H).

(b) A solution of  $\alpha$ -isopropylamino- $\alpha$ -(3,4-dimethoxyphenyl)acetonitrile (5) (5 g, 0.02 mol) in ethanol (40 ml) at room temperature was treated with a slow stream of H<sub>2</sub>S for 4 h. The reaction flask was sealed and left at ambient temperature for 16 h. The solid was removed, washed with ethanol and dried to give the dimer of the title compound as a pale yellow powder (3.4 g, 87%), m.p. 115° (Found: C, 59.2; H, 5.7%; *m/e*, 335. C<sub>18</sub>H<sub>20</sub>S<sub>2</sub>O<sub>4</sub> requires C, 59.3; H, 5.5%; *M*, 364),  $\delta$  3.8br (12H, OCH<sub>3</sub>), 4.5br (2H, CHS), and 6.6br (6H, aromatic H).

*Reaction of Veratraldehyde with Hydrogen Sulphide*.—Veratraldehyde was treated with hydrogen sulphide by the standard procedure described for  $\alpha$ -amino-nitriles and gave a mixture of bis-(3,4-dimethoxybenzyl) disulphide, g.l.c. (2% OV1, 240°) *R<sub>t</sub>* 3.5 min and bis-(3,4-dimethoxybenzyl) polysulphides;  $\delta$  3.56 ( $\alpha$ -CH<sub>2</sub>, disulphide) and  $\delta$  3.96, 4.07, and 4.12 ( $\alpha$ -CH<sub>2</sub>, polysulphides) shown by integration to be in the ratio 2 : 5 [Found: C, 52.6; H, 5.6; S, 26.5. Calc. for (C<sub>9</sub>H<sub>11</sub>O<sub>2</sub>)<sub>2</sub>S<sub>3.4</sub>: • C, 52.55; H, 5.4; S, 26.5%].

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• Established from n.m.r. integrals of  $\alpha$ -CH<sub>2</sub> polysulphide signals assigned as follows:  $\delta$  3.56 [disulphide (27%)], 3.96 [trisulphide (27.5%)], 4.07 [tetrasulphide (22.5%)], and 4.12 [pentasulphide (22.5%)].