

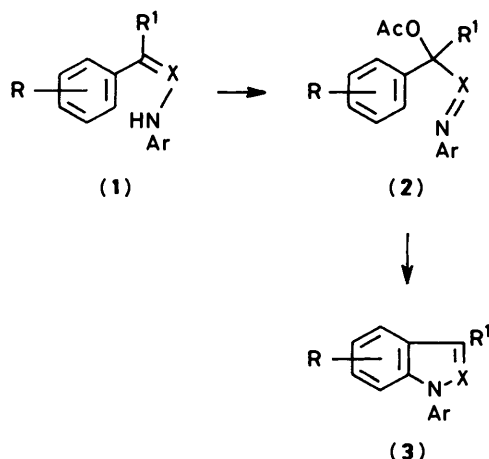
## Polarized Ketene *S,S*- and *S,N*-Acetals. Part 52.<sup>1</sup> Lead Tetra-acetate Oxidation of 3-Anilino-3-methylthio-2-arylacrylonitriles. A Novel Approach to Substituted Indoles

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Lead tetra-acetate oxidation of 3-anilino-3-methylthio-2-phenylacrylonitrile (**4a**) gave the iminoacetate (**5a**) and 3-cyano-2-methylthio-1-phenylindole (**6a**). The corresponding methoxy substituted 2-arylacrylonitriles (**4b–d**), however, yielded the symmetric dimeric products (**7a–c**) and the unstable iminoacetates (**5a–d**) respectively under similar conditions. The corresponding *p*-chloro derivative (**4e**) afforded the stable iminoacetate (**5e**), dimer (**7d**), and 6-chloroindole (**6e**) in low yields. The iminoacetates (**5a–e**) could be cyclized to the respective indoles (**6a–e**) in the presence of boron trifluoride–diethyl ether. The probable mechanistic pathways for the formation of various products are described.

Lead tetra-acetate oxidation of some enamines has been reported in the literature<sup>2</sup> to yield a variety of cleavage products arising from the initially formed diacetates. The aminofumarates, which can be considered as enamine analogues have also been reported<sup>3</sup> to undergo similar oxidation to give a number of interesting dimeric and heterocyclic products. However, the enamines (**1**; X = CR<sup>2</sup>) carrying  $\beta$ -aryl groups are of particular interest, since the intermediate iminoacetates (**2**; X = CR<sup>2</sup>) derived from such systems would be expected to undergo Lewis acid catalysed cyclization with possible aromatic ring participation to yield the indole derivatives (**3**; X = CR<sup>2</sup>) (Scheme 1). From our literature survey, we found that



Scheme 1.

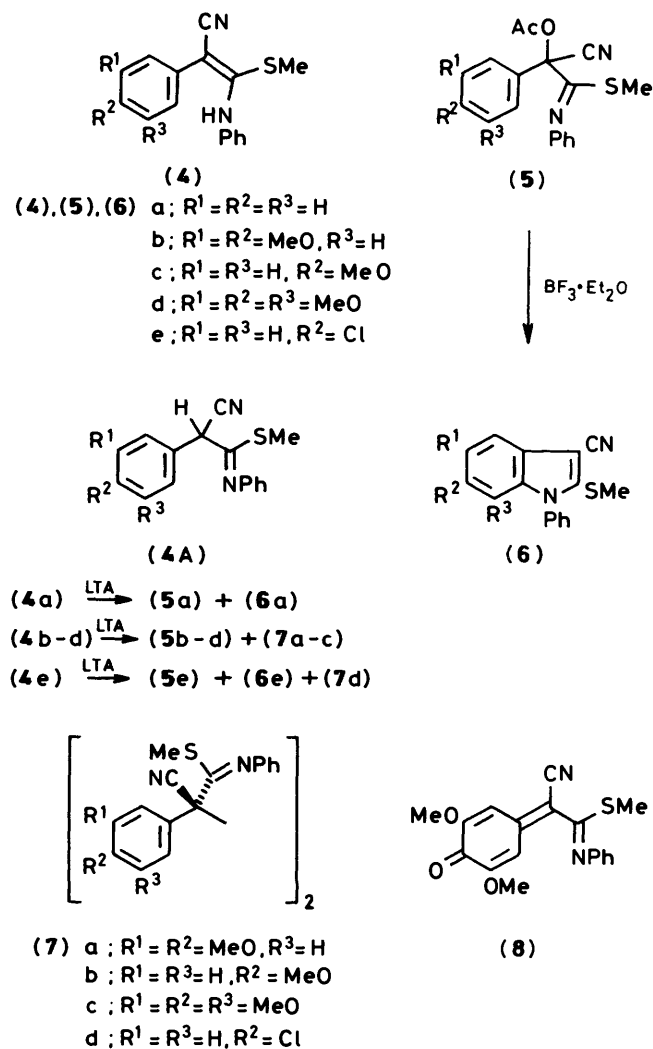
analogous systems such as arylhydrazones (**1**; X = N) derived from aromatic ketones, have indeed been shown<sup>4</sup> to undergo lead tetra-acetate oxidations to give indazoles (**3**; X = N) in the presence of a Lewis acid (Scheme 1). We therefore decided to investigate whether the polarized ketene *S,N*-acetals (**4**) derived from arylacetonitriles would yield the corresponding indole derivatives under similar oxidation conditions. We now report our results on these studies.

### Results and Discussion

The previously unreported *S,N*-acetals (**4a–e**) selected for the present studies were prepared by the known procedure<sup>5</sup> from the respective arylacetonitriles. From the <sup>1</sup>H n.m.r. data of (**4a–e**), it was found that they exist exclusively in the enamino tautomeric form rather than the corresponding imino form (**4A**). When the *S,N*-acetal (**4a**) was oxidized with lead tetra-acetate in dichloromethane at room temperature, work-up and column chromatography of the reaction mixture afforded two products, which were characterized as the indole (**6a**) (30%) and the iminoacetate (**5a**) (43%) (Scheme 2) on the basis of spectral and analytical data (see Experimental section). The yield of indole (**6a**) could be improved to 40%, when compound (**4a**) was added slowly (over 15 min) to lead tetra-acetate. Subsequently, when compound (**5a**) was treated with boron trifluoride–diethyl ether in refluxing benzene, the corresponding indole (**6a**) was obtained in 90% yield (mixed m.p. and superimposable i.r. and n.m.r. spectra).

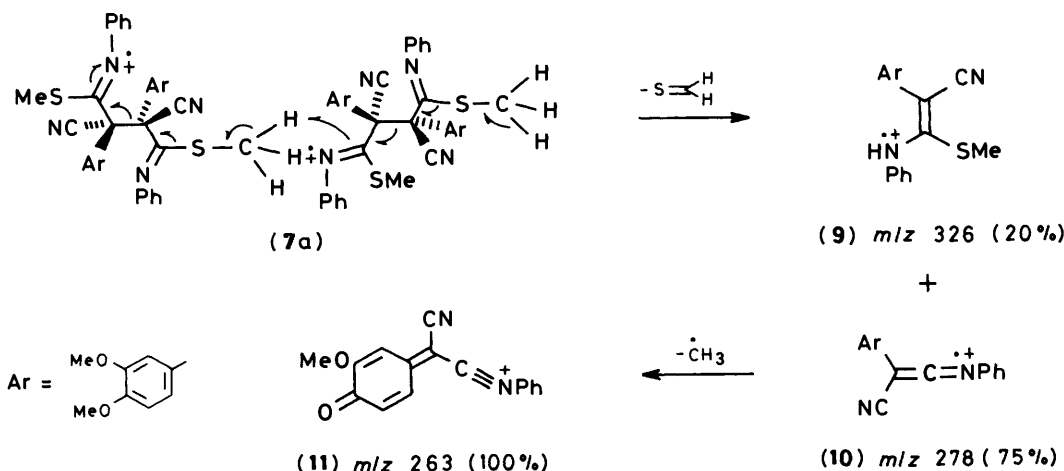
The *S,N*-acetals (**4b–d**) derived from the corresponding methoxy substituted arylacetonitriles were next examined. The presence of electron-donating groups was considered to facilitate the oxidative cyclization to indole. However, when compound (**4b**) was oxidized with lead tetra-acetate under identical conditions, work-up of the reaction mixture gave a light coloured amorphous solid, which was characterized as the dimer (**7a**), while the viscous residue obtained after concentration of the filtrate was identified as crude iminoacetate (**5b**) on the basis of its i.r. and n.m.r. spectra. Our attempts to purify (**5b**) were unsuccessful and yielded only an intractable mixture of several products. However, when the crude iminoacetate (**5b**) was cyclized in the presence of boron trifluoride–diethyl ether, the corresponding 5,6-dimethoxyindole (**6b**) was obtained in good yield. The spectral and analytical data of compounds (**6b**) and (**7a**) were in agreement with the assigned structures (see Experimental section). The high resolution mass spectrum of (**7a**) did not exhibit a molecular ion peak, the prominent peaks observed in the spectrum were assigned to the fragments (**9**), (**10**), and (**11**) (Scheme 3). The <sup>13</sup>C n.m.r. spectrum of compound (**7a**) showed a signal due to an sp<sup>3</sup> quaternary  $\beta$ -carbon at  $\delta$  64.5 (s), which further supported its structure.

Similar oxidation studies of compounds (**4c**) and (**4d**) under identical conditions also yielded the mixtures of the corresponding dimers (**7b**), (**7c**) and the crude iminoacetates (**5c**) and (**5d**) respectively (Scheme 2). Attempted purification of



Scheme 2.

compound (5c) by column chromatography (silica gel) yielded only a complex mixture of products, while compound (5d) gave a bright yellow product which was characterized as the quinonemethide (8).<sup>\*</sup> The crude compounds (5c) and (5d) were



Scheme 3.

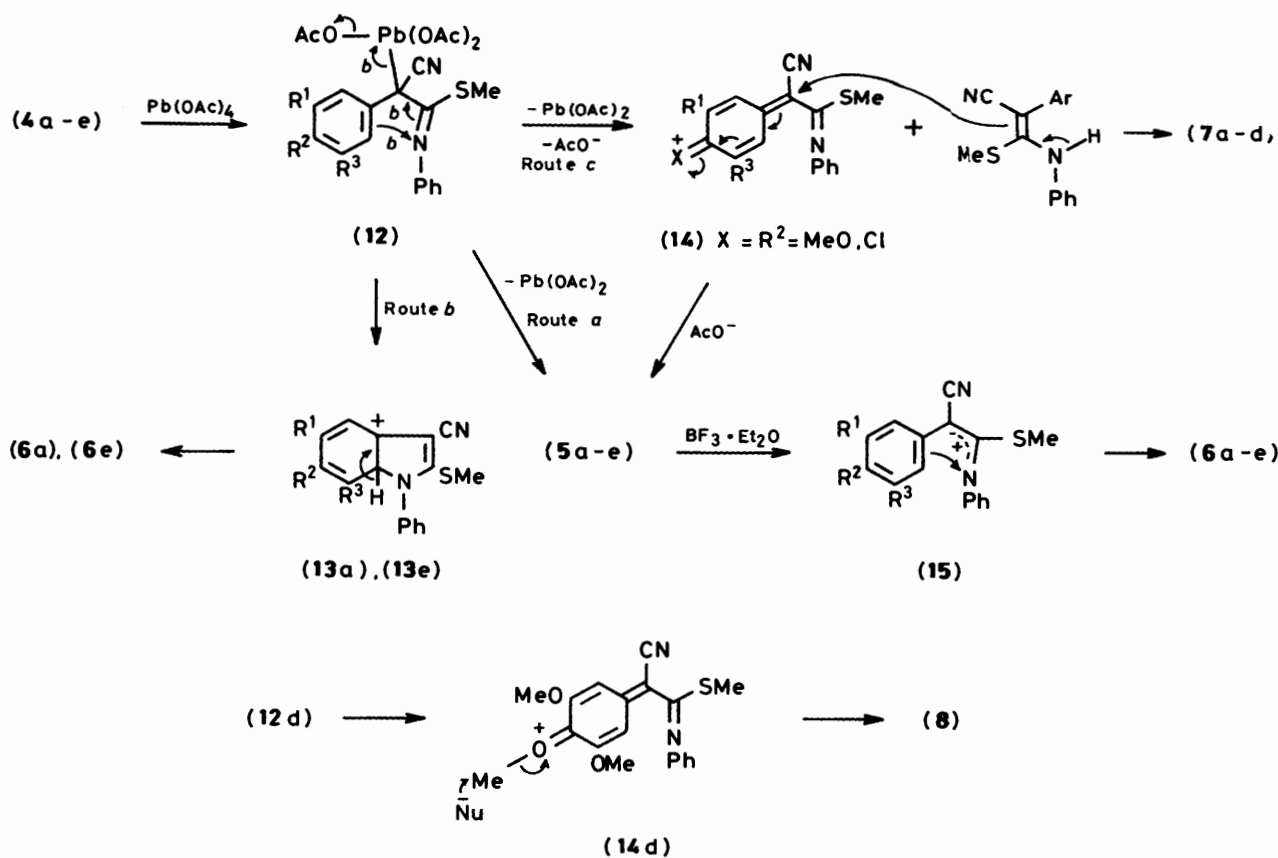
subjected to further cyclization in the presence of boron trifluoride-diethyl ether, when the corresponding 6-methoxy-(6c) and 5,6,7-trimethoxy-indoles (6d) were obtained in good yields. The spectral and analytical data of compound (6c), (6d), (7b), (7c), and (8) were in agreement with the assigned structures (see Experimental section).

When the *p*-chloro *S,N*-acetal (4e) was oxidized with lead tetra-acetate under similar reaction conditions, product analysis showed the formation of three compounds (t.l.c.), which were characterized, after isolation, as the dimer (7d) (13%), 6-chloroindole (6e) (9%), and the iminoacetate (5e) (62%) on the basis of spectral and analytical data. Efforts to improve the yield of compound (6e) directly were unsuccessful. Subsequently, the corresponding acetate (5e) was treated with boron trifluoride-diethyl ether in refluxing benzene (10 h), when compound (6e) was obtained in comparatively lower yield (54%). This is probably due to the partial deactivating effect of chlorine atom.

**Mechanistic Considerations.**—The probable mechanistic pathways for the formation of various products from the *S,N*-acetals (4) are shown in Scheme 4. The initially formed C-plumbylated adduct (12) appears to be a common intermediate from which compounds (5), (6), and (7) could be derived depending on the nature of the substituent in the *para*-position (R<sup>2</sup>). Thus the formation of iminoacetates (5a–e) by intramolecular decomposition of the adduct (12) is a common pathway for all the *S,N*-acetals (4a–e) (Route a). The plumbylated adduct (12) undergoes oxidative cyclization to indole (6a) [or (6e)] when R<sup>2</sup> = H or Cl (Route b). However when R<sup>2</sup> is an electron-donating group like MeO or Cl, the C-plumbylated adduct (12) appears to cleave with the assistance of the electron-donating group to give the corresponding quinonemethide intermediate (14) (Route c), which in turn is attacked by unchanged *S,N*-acetal (4) to give the dimeric products (7) in varying yields.<sup>†</sup> The quinonemethide (8) is

<sup>\*</sup> The quinonemethide (8) was also obtained, when the crude iminoacetate (5d) was left at room temperature for a few days. It remained unchanged on prolonged refluxing in benzene in the presence of boron trifluoride-diethyl ether.

<sup>†</sup> The quinonemethide intermediate (14) could alternatively be attacked by acetate ion to give iminoacetate (5b–e). This point has been confirmed by experimental work. When the *S,N*-acetal (4b) was added in one proton to a suspension of lead tetra-acetate, the yield of dimer was found to be a minimum (22%), although it increased (41%) when the *S,N*-acetal (4b) was added in portions over a long period (20 min).



Scheme 4.

plausibly formed from iminoacetate (5d) via intermediate (14d) ( $X = \text{MeO}$ ) by facile demethylation by some nucleophilic species present in the reaction mixture due to steric crowding in the aromatic ring (Scheme 4).

In summary, lead tetra-acetate oxidation of *S,N*-acetals (4a-e) yields an interesting series of products. The formation of indole derivatives (6a-e) from compounds (4a-e) respectively represents a novel approach to hitherto unreported indole derivatives. The polarized ketene *S,N*- and *N,N*-acetals, which are readily available from a wide variety of active methylene compounds could make this method useful for the synthesis of large structural variants of indoles and related studies are currently in progress.

### Experimental

M.p.s were determined on a 'Thomas Hoover' Capillary m.p. apparatus and are uncorrected. I.r. spectra were obtained on a Perkin-Elmer 297 spectrophotometer. N.m.r. spectra were recorded on Varian EM-390 (90 MHz) machine. The  $^{13}\text{C}$  n.m.r. and mass spectra were obtained from Regional Sophisticated Instrumentation Centres at the Indian Institute of Science, Bangalore and the Central Drug Research Institute, Lucknow respectively.

**Preparation of 3-Anilino-3-methylthio-2-arylacrylonitriles (4a-e).**—The new compounds (4a-e) were prepared by an earlier reported procedure,<sup>5</sup> by treatment of the respective arylacetonitriles with sodium hydride and phenyl isothiocyanate in dimethylformamide followed by methylation with methyl iodide.

**3-Anilino-3-methylthio-2-phenylacrylonitrile (4a).** Light yellow crystals (benzene-hexane) (84%), m.p. 118–119 °C;  $\nu_{\text{max}}$  (KBr) 3 290 (NH) and 2 200  $\text{cm}^{-1}$  (CN);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.20 (3 H, s, SMe), 6.45 (1 H, s, NH), 6.90–7.40 (10 H, m, ArH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 15.7 (SMe), 92.36 (NCC=), 123.4 (C≡N), 119.9, 127.2, 127.4, 128.2, 128.7, 128.9, 133.2, 139.8 (ArC), and 153.1 [ $=\text{C}(\text{SMe})\text{NH}$ ] (Found: C, 72.4; H, 5.15; N, 10.75.  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{S}$  requires C, 72.18; H, 5.26; N, 10.53%).

**3-Anilino-2-(3,4-dimethoxyphenyl)-3-methylthioacrylonitrile (4b).** Yellow crystals (benzene-hexane) (74%), m.p. 172–173 °C;  $\nu_{\text{max}}$  (KBr) 3 300 (NH) and 2 190  $\text{cm}^{-1}$  (CN);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.29 (3 H, s, SMe), 3.65 (3 H, s, OMe), 3.80 (3 H, s, OMe), 6.35 (1 H, s, NH), and 6.60–7.30 (8 H, m, ArH);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 15.7 (SMe), 55.5, 55.7 (OMe), 93.5 [ $=\text{C}(\text{CN})$ ], 120.3 (C≡N), 110.6, 111.2, 119.7, 120.2, 123.4, 125.8, 129.1, 140.2, 148.2, 148.8 (ArC), and 151.9 [ $=\text{C}(\text{SMe})\text{NHPh}$ ] (Found: C, 66.45; H, 5.65; N, 8.45.  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$  requires C, 66.25; H, 5.52; N, 8.59%).

**3-Anilino-2-(4-methoxyphenyl)-3-methylthioacrylonitrile (4c).** Yellow crystals (benzene-hexane) (70%), m.p. 106–108 °C;  $\nu_{\text{max}}$  (KBr) 3 240 (NH) and 2 190  $\text{cm}^{-1}$  (CN);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.18 (3 H, s, SMe), 3.70 (3 H, s, OMe), 6.20 (1 H, s, NH), and 6.60–7.40 (9 H, m, ArH) (Found: C, 68.7; H, 5.5; N, 9.6.  $\text{C}_{17}\text{H}_{16}\text{N}_2\text{OS}$  requires C, 68.92; H, 5.41; N, 9.46%).

**3-Anilino-3-methylthio-2-(3,4,5-trimethoxyphenyl)acrylonitrile (4d).** Yellow crystals (benzene-hexane) (80%), m.p. 144–145 °C;  $\nu_{\text{max}}$  (KBr) 3 140 (NH) and 2 200  $\text{cm}^{-1}$  (CN);  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.25 (3 H, s, SMe), 3.65 (6 H, s, OMe), 3.75 (3 H, s, OMe), 6.55 (2 H, s, ArH), and 6.82–7.32 (6 H, m, ArH and NH) (Found: C, 64.2; H, 5.55; N, 7.85.  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$  requires C, 64.04; H, 5.62; N, 7.87%).

**3-Anilino-2-(4-chlorophenyl)-3-methylthioacrylonitrile**

(4e). Yellow crystals (benzene-hexane) (60%), m.p. 148–149 °C;  $\nu_{\max}$ (KBr) 3 280 (NH) and 2 190  $\text{cm}^{-1}$  (CN);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 2.15 (3 H, s, SMe), 6.10 (1 H, s, NH), and 6.70–7.35 (9 H, m, ArH) (Found: C, 63.7; H, 4.4; N, 9.2.  $\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{S}$  requires C, 63.89; H, 4.33; N, 9.32%).

**Lead Tetra-acetate Oxidation of compounds (4a–e): General Procedure for (4a).**—A solution of the *S,N*-acetal (4a) (4.0 g, 15 mmol) in dichloromethane (80 ml) was added (over 1 min) to a well-stirred suspension of lead tetra-acetate (6.9 g, 15.5 mmol) in dichloromethane (20 ml) at 0 °C. The reaction mixture was stirred for a further 30 min at room temperature and the precipitated lead diacetate was filtered off and washed with dichloromethane (100 ml). The filtrate was washed with water (3 × 100 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to give a brownish residue, which was subjected to column chromatography over silica gel. Elution with hexane-ethyl acetate (9:1) gave first the indole (6a) as a white crystalline solid (hexane-chloroform) (1.10 g, 30%), m.p. 78–79 °C;  $\nu_{\max}$ (KBr) 2 200  $\text{cm}^{-1}$  (C≡N);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 2.45 (3 H, s, SMe) and 6.85–7.80 (9 H, m, ArH);  $\delta_{\text{C}}$ ( $\text{CDCl}_3$ ) 90.8 (C-3), 115.4 (CN), 127.3 (C-9), 135.4 (C-1' of *N*-phenyl), 137.6 (C-8), 142.7 (C-2), 110.9, 118.5, 122.4, 124.2, 127.8, 129.2, and 129.5 (ArC) (Found: C, 72.85; H, 4.4; N, 10.7.  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{S}$  requires C, 72.73; H, 4.55; N, 10.61%);  $m/z$  264 ( $M^+$ , 100). Further elution gave the iminoacetate (5a) (2.1 g, 43%) as a white crystalline solid (hexane-chloroform), m.p. 80–81 °C;  $\nu_{\max}$ (KBr) 2 200 (w, C≡N) and 1 758  $\text{cm}^{-1}$  (C=O);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 1.78 (3 H, s, SMe), 2.26 (3 H, s, MeCO), and 6.70–7.91 (10 H, m, ArH);  $\delta_{\text{C}}$ ( $\text{CDCl}_3$ ) 15.6 (SMe), 20.8 ( $\text{CH}_3\text{CO}$ ), 79.3 (COAc), 115.9 (C≡N), 118.9, 124.3, 128.1, 129.0, 129.6, 130.0, 133.1, 146.9 (ArC), 159.1 (N=C SMe), and 168.3 (MeC=O);  $m/z$  324 ( $M^+$ , 70%), 266 ( $M^+ - 58$ , 75) (Found: C, 66.45; H, 4.85; N, 8.80.  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$  requires C, 66.67; H, 4.94; N, 8.64%).

When the *S,N*-acetal was added slowly dropwise (over 20 min) to the lead tetra-acetate suspension, the yield of the indole (6a) was increased to 40% (1.50 g) and iminoacetate (5a) was obtained in 35% yield (1.70 g).

**Lead Tetra-acetate of Compound (4b).**—Oxidation of compound (4b) (4.90 g, 15 mmol) and work-up of the reaction mixture as above gave a yellowish brown viscous residue which on trituration with hexane gave the dimer (7a) (1.1 g, 22%) as a pale coloured amorphous solid (hexane-chloroform), m.p. 156–157 °C;  $\nu_{\max}$ (KBr) NH absent 2 200 (w, C≡N) and 1 600  $\text{cm}^{-1}$  (C=N);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 1.85 (3 H, s, SMe), 3.70 (3 H, s, MeO), 3.85 (3 H, s, MeO), and 6.75–7.82 (8 H, m, ArH);  $\delta_{\text{C}}$ ( $\text{CDCl}_3$ ) 16.58 (SMe), 55.68 (MeO), 55.85 (MeO), 64.5 (NCC, s), 117.6 (C=N, s), 110.3, 112.5, 119.4, 122.41, 123.0, 124.5, 129.1, 146.8, 148.1, 149.8 (ArC), and 158.5 (CNPh) (Found: C, 66.35; H, 5.35; N, 8.7.  $\text{C}_{36}\text{H}_{34}\text{N}_4\text{O}_4\text{S}_2$  requires C, 66.46; H, 5.23; N, 8.62%).

The mother liquor obtained after filtration of compound (7a) was evaporated under reduced pressure to give an orange-brown viscous residue which was found to be crude iminoacetate (5b) (3.5 g);  $\nu_{\max}$ (neat) 1 760 (CO) and 2 200  $\text{cm}^{-1}$  (w, C≡N);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 1.80 (s, SMe), 2.08 (s, MeCO), 3.65 (s, MeO), 3.82 (s, MeO), and 6.70–7.75 (m, ArH).

**Boron Trifluoride-Diethyl Ether Catalysed Cyclisation of Compound (5b).**—3-Cyano-5,6-dimethoxy-2-methylthio-1-phenylindole (6b). The crude iminoacetate (5b) (3.4 g) from compound (4b), dry ether (50 ml), and  $\text{BF}_3\text{-Et}_2\text{O}$  (5 ml) was refluxed for 0.5 h then poured over cold water and extracted with chloroform (2 × 50 ml). The chloroform extract was washed with aqueous sodium hydrogen carbonate (100 ml), water (2 × 100 ml), dried, and evaporated to give a viscous residue, which was chromatographed on silica gel using hexane-benzene (4:1) as eluant to give the indole (6b) [2.40 g, 83% from (5b); 49% from (4b)] as light yellow crystals (benzene-

hexane), m.p. 146–147 °C;  $\nu_{\max}$ (KBr) 2 200  $\text{cm}^{-1}$  (CN);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 2.34 (1 H, s, SMe), 3.78 (3 H, s, OMe), 3.90 (3 H, s, OMe), 6.52 (1 H, s, 7-H), 7.13 (1 H, s, 4-H), and 7.22–7.80 (5 H, m, ArH);  $\delta_{\text{C}}$ ( $\text{CDCl}_3$ ) 18.8 (SMe), 56.1, 56.2 (OMe), 92.0 (C-3, s), 94.1, 99.1 (C-4, C-7), 115.5 (CN), 120.2 (C-9), 127.9, 129.0, 129.5 (ArC), 132.3 (C-8), 135.9 (C-2), 139.1 (C<sup>1</sup> of *N*-phenyl), 147.3, and 148.8 (C-5, C-6);  $m/z$  324 ( $M^+$ , 100%) and 309 ( $M^+ - \text{Me}$ , 90) (Found: C, 66.55; H, 4.7; N, 8.7.  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$  requires C, 66.67; H, 4.94; N, 8.64%).

**Lead Tetra-acetate Oxidation of Compound (4c).**—Oxidation of compound (4c) (4.5 g, 15 mmol) as described for compound (4b) gave the dimer (7b) (1.2 g, 26%) as a pale coloured amorphous solid (hexane-benzene), m.p. 140 °C;  $\nu_{\max}$ (KBr) 2 195 (w, C≡N) and 1 605  $\text{cm}^{-1}$  (C=N);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 1.82 (3 H, s, SMe), 3.80 (3 H, s, OMe), and 6.80–7.70 (9 H, m, ArH);  $\delta_{\text{C}}$  16.6 (SMe), 55.5 (MeO), 65.2 (CCN, s), 117.8 (s, CN), 113.8, 119.8, 123.2, 125.1, 129.1, 131.2, 147.1, 158.6 (ArC), and 160.8 (C=NPh);  $m/z$  296 (20), 248 (72), and 233 (100) (Found: C, 69.25; H, 5.2; N, 9.35.  $\text{C}_{34}\text{H}_{30}\text{N}_4\text{O}_2\text{S}_2$  requires C, 69.15; H, 5.08; N, 9.49%).

The mother liquor obtained after filtration of compound (7b) was evaporated to give crude iminoacetate (5c) (3.8 g) [ $\nu_{\max}$ (neat) 1 760  $\text{cm}^{-1}$ ] which was cyclized in the presence of  $\text{BF}_3\text{-Et}_2\text{O}$  as described for (5b) to give 3-cyano-6-methoxy-2-methylthio-1-phenylindole (6c) (2.5 g) [79% from (5c) and 56% from (4c)] as white crystals (hexane-benzene), m.p. 114–115 °C;  $\nu_{\max}$ (KBr) 2 210  $\text{cm}^{-1}$  (CN);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 2.40 (3 H, s, SMe), 3.65 (3 H, s, OMe), 6.36 (1 H, d, *J* 2.5 Hz, 7-H), 6.80 (1 H, dd, *J* 2.5 and 7 Hz, 5-H), and 7.20–7.67 (6 H, m, 4-H and ArH);  $m/z$  294 ( $M^+$ , 100) and 279 ( $M^+ - \text{Me}$ , 90) (Found: C, 69.25; H, 4.9; N, 9.35.  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{OS}$  requires C, 69.39; H, 4.76; N, 9.52%).

**Lead Tetra-acetate Oxidation of Compound (4d).**—Oxidation of compound (4d) (5.40 g, 15 mmol) as described for (4a) gave dimer (7c) as a white amorphous solid (0.95 g, 16%), m.p. 174–175 °C;  $\nu_{\max}$ (KBr) 2 200  $\text{cm}^{-1}$  (w, C≡N);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 3.85 (3 H, s, OMe), 6.60 (2 H, s, ArH), and 6.90–7.60 (5 H, m, ArH);  $m/z$  356 (10%), 317 (70) and 293 (100) (Found: C, 64.1; H, 5.45; N, 7.75.  $\text{C}_{38}\text{H}_{38}\text{N}_4\text{O}_6\text{S}_2$  requires C, 64.22; H, 5.35; N, 7.89%).

Evaporation of the filtrate from compound (7c) gave crude iminoacetate (5d) (4.90 g);  $\nu_{\max}$ (neat) 1 758  $\text{cm}^{-1}$  which on cyclization in the presence of boron trifluoride-diethyl ether as described for compound (5b) gave 3-cyano-5,6,7-trimethoxy-2-methylthio-1-phenylindole (6d) (3.4 g) [80% from (5d); 64% from (4d)] as light yellow crystals (hexane-benzene), m.p. 151–152 °C;  $\nu_{\max}$ (KBr) 2 211  $\text{cm}^{-1}$  (C≡N);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 2.40 (3 H, s, MeS), 3.35 (3 H, s, 7-MeO), 3.81 (3 H, s, MeO), 3.89 (3 H, s, MeO), 6.95 (1 H, s, 4-H), and 7.25–7.60 (5 H, m, ArH);  $\delta_{\text{C}}$ ( $\text{CDCl}_3$ ) 18.5 (SMe), 56.1, 61.15, 61.20 (OMe), 91.5 (C-3), 95.3 (C-4), 115.5 (CN), 124.2 (C-9), 125.7 (C-8), 128.4, 128.8, 128.9 (ArC), 137.7 (C-2), 140.2, 140.6, 142.3, and 151.1 (C-5, C-6, C-7, and C<sup>1</sup> of *N*-phenyl);  $m/z$  356 ( $M^+$ , 100%) and 341 ( $M^+ - \text{Me}$ , 90) (Found: C, 64.7; H, 5.2; N, 8.3.  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2\text{S}$  requires C, 64.40; H, 5.08; N, 7.91%).

In another experiment, the crude iminoacetate (2.0 g) was passed through a silica gel column (benzene-hexane) to give the quinonemethide (8) as yellow crystals (from benzene-hexane) [1.0 g, 62% from (5d)], m.p. 137–138 °C;  $\nu_{\max}$ (KBr) 2 200 (C≡N), 1 660 (C=O), and 1 580  $\text{cm}^{-1}$  (C=N);  $\delta_{\text{H}}$ ( $\text{CDCl}_3$ ) 2.58 (3 H, s, SMe), 3.75 (3 H, s, OMe), 3.80 (3 H, s, OMe), 6.1 (1 H, br s, quinone H), 6.35 (1 H, br s, quinone H), and 6.70–7.38 (5 H, m, ArH);  $m/z$  340 ( $M^+$ , 100%), 293 ( $M^+ - 47.80$ );  $\lambda_{\max}$ (EtOH), 355 (log  $\epsilon$  3.19), and 390sh nm (1.54) (Found: C, 63.65; H, 4.6; N, 8.05.  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$  requires C, 63.52; H, 4.71; N, 8.24%).

**Lead Tetra-acetate Oxidation of Compound (4e).**—Oxidation of (4e) (4.5 g, 15 mmol) as described for compound (4b) gave the dimer (7d) (0.6 g, 13%) as an amorphous solid, m.p. 166–

167 °C;  $\nu_{\max}(\text{KBr})$  2 240 (w, C≡N) and 1 639  $\text{cm}^{-1}$  (C=N);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.80 (3 H, s, SMe) and 7.0–7.50 (9 H, m, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  16.6 (SMe), 65.0 (CCN), 117.1 (C≡N), 119.8, 125.4, 128.8, 129.2, 130.0, 131.1, 136.5, 146.5 (ArC), 157.8 (C=N);  $m/z$  300, 302 (15.8) and 252, 254 (100) (Found: C, 64.25; H, 4.15; N, 9.2.  $\text{C}_{32}\text{H}_{24}\text{Cl}_2\text{N}_4\text{S}_2$  requires C, 64.11; H, 4.01; N, 9.35%).

Evaporation of the filtrate from compound (7d) gave a viscous residue (4.3 g) which was column chromatographed over silica gel. Elution with ethyl acetate–hexane (1:9) gave first 6-chloro-3-cyano-2-methylthio-1-phenylindole (0.4 g, 9%) as white crystals, m.p. 87–88 °C;  $\nu_{\max}(\text{KBr})$  2 215  $\text{cm}^{-1}$  (C≡N);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.45 (3 H, s, SMe) and 7.2–8.3 (8 H, m, ArH);  $m/z$  300 and 298 ( $M^+$ , 30, 80) (Found: C, 64.55; H, 3.85; N, 9.6.  $\text{C}_{16}\text{H}_{11}\text{ClN}_2$  requires C, 64.32; H, 3.69; N, 9.38%).

Further elution with ethyl acetate–hexane (1:9) yielded iminoacetate (5e) as white crystals (hexane–dichloromethane) (2.20 g, 62%), m.p. 115–116 °C;  $\nu_{\max}(\text{KBr})$  2 240 (w, C≡N), 1 765 (CO), and 1 630  $\text{cm}^{-1}$  (C=N);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.80 (3 H, s, SMe), 2.20 (3 H, s, MeCO), and 6.75–7.80 (9 H, m, ArH);  $m/z$  358, 360 ( $M^+$ , 80, 35%) 300, 298 ( $M^+$  – MeC=O, 100, 85) (Found: C, 60.35; H, 4.3; N, 7.65.  $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{O}_2\text{S}$  requires C, 60.25; H, 4.18; N, 7.81%).

**Boron Trifluoride-Diethyl Ether Catalysed Cyclizations of Compounds (5a) and (5e).**—A solution of compound (5a) (1.6 g, 5 mmol) in benzene (20 ml) and  $\text{BF}_3\text{-Et}_2\text{O}$  (5 ml) was refluxed for 2 h. Work-up of the reaction mixture as for (5b) gave the

indole (6a) (1.0 g, 78%) (mixed m.p. superimposable i.r. and n.m.r.).

Cyclization of compound (5e) (1.8 g, 5 mmol) under similar conditions after refluxing for 10 h gave indole (6e) (0.8 g, 54%) (superimposable i.r. and n.m.r. spectra).

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#### References

- Part 51, C. V. Asokan, H. Ila, and H. Junjappa, *Synthesis*, 1987, 284.
- (a) F. Corbani, B. Rindone, and C. Scolastico, *Tetrahedron*, 1973, **29**, 3253; (b) F. Corbani, B. Rindone, and C. Scolastico, *ibid.*, 1975, **31**, 455.
- (a) S. K. Khetan, *J. Chem. Soc., Chem. Commun.*, 1972, 917; (b) R. M. Carr, R. O. C. Norman, and J. M. Vernon, *ibid.*, 1977, 854; (c) R. M. Carr, R. O. C. Norman, and J. M. Vernon, *J. Chem. Soc., Perkin Trans. 1*, 1980, 156; (d) J. M. Vernon, R. M. Carr, and M. A. Sukari, *J. Chem. Res.*, 1982, (S) 115; (M) 1310.
- (a) W. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc.*, 1965, 3048; (b) *ibid.*, 5177; (c) *ibid.*, 1966, 1527; (d) N. Vivona, V. Frenna, S. Buscemi, and M. Condor, *J. Heterocycl. Chem.*, 1985, **22**, 29.
- A. Kumar, V. Aggarwal, H. Ila, and H. Junjappa, *Synthesis*, 1980, 748.

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