

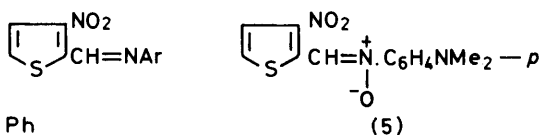
Condensed Thiophen Ring Systems. Part 21.¹ 5-Arylthieno[3,2-*c*]pyrazoles and Attempted Preparation of 5-Arylthieno[2,3-*c*]pyrazoles, resulting in a Novel Thiophen to Pyrrole Transformation

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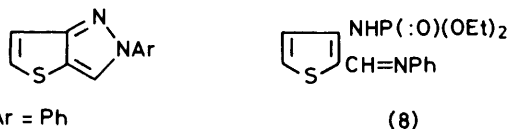
Whereas reductive cyclisation of the *o*-nitro-anils (1) and (2) with triethyl phosphite gave the corresponding 5-arylthieno[3,2-*c*]pyrazoles (6) and (7), respectively, similar treatment of the *o*-nitro-anils (14) and (15) gave, unexpectedly, the 1-arylpyrrole-3-carbonitriles (16) and (17), respectively, as the only isolable products. Convenient syntheses of 3-nitrothiophen-2- and 2-nitrothiophen-3-carbaldehyde are described.

In examining the scope of our synthesis of thienopyrazoles¹ we have studied reactions of the anils (1), (2), (14), and (15) with triethyl phosphite.

2-Methyl-3-nitrothiophen condensed with *NN*-dimethyl-4-nitrosoaniline to give a mixture of the anil (2) and the nitrone (5) (ratio 1 : 5.25, as determined from



- (1) Ar = Ph
 (2) Ar = C₆H₄NMe₂ - *p*
 (3) Ar = C₆H₄Me - *p*
 (4) Ar = C₆H₄Cl - *p*



- (6) Ar = Ph
 (7) Ar = C₆H₄NMe₂ - *p*

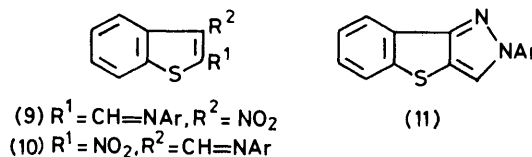
the methine proton signals in the ¹H n.m.r. spectrum of the mixture) (*cf.* ref. 1). Selective hydrolysis of the anil (2) in this mixture was achieved with 3*M*-sulphuric acid and the nitrone (5) was separated readily from the resulting mixture of nitrone and 3-nitrothiophen-2-carbaldehyde by extraction with ether (*cf.* ref. 1). Hydrolysis of the nitrone-anil mixture with concentrated hydrochloric acid gave exclusively 3-nitrothiophen-2-carbaldehyde. This provides a more convenient synthesis of this aldehyde than that reported previously.² For the synthesis of 2-methyl-3-nitrothiophen from 2-methylthiophen we found Synder's route³ preferable (higher overall yields and more convenient) to that of Gronowitz.⁴

3-Nitrothiophen-2-carbaldehyde was condensed with several aromatic amines to give the anils (1)–(4); all but anil (2) were unstable in light.

Treatment of the parent anil (1) with triethyl phosphite in *t*-butylbenzene (ratio 1 : 3) gave 5-phenylthieno[3,2-*c*]pyrazole (6) together with the phosphoramidate (8). The phosphoramidate, which was separated from compound (6) by fractional crystallisation, did not give a satisfactory elemental analysis, but was characterised adequately by its spectroscopic properties (see Experi-

mental section). It arises presumably by hydrolysis of the corresponding phosphorimidate believed to be formed by trapping an intermediate nitrene. With triethyl phosphite, anil (2) similarly gave the 5-arylthieno[3,2-*c*]pyrazole (7) as the only isolable product. The dimethylamino-group present resulted in a higher yield of the cyclised product.⁵

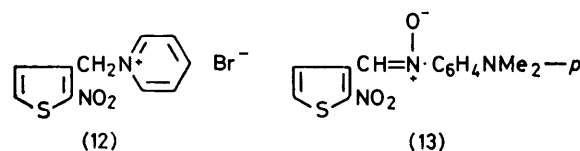
Whereas anils with the general structure (9), derived



- (9) R¹ = CH=NAr, R² = NO₂
 (10) R¹ = NO₂, R² = CH=NAr

from 3-nitrobenzo[*b*]thiophen-2-carbaldehyde, undergo reductive cyclisation in the presence of a trivalent phosphorus reagent to give the corresponding 2-aryl[1]-benzothieno[3,2-*c*]pyrazole (11), similar treatment of the isomeric anils (10) yields a mixture of the corresponding 2-aryl[1]benzothieno[2,3-*c*]pyrazole and benzo[*b*]thiophen-3-carbonitrile.⁵ Formation of the nitrile was rationalised⁵ by invoking an interesting ring-opening–ring-closure sequence of reactions for the thiophen rings. It was of interest, therefore, to study the behaviour of the analogous thiophen anils in this reaction.

The required starting material, 2-nitrothiophen-3-carbaldehyde, has been prepared previously in low yield by bromination of 3-methyl-2-nitrothiophen⁶ with *N*-bromosuccinimide and conversion of the 3-bromo-methyl compound into the 3-hydroxymethyl compound, which was oxidised to the nitro-aldehyde by *N*-bromosuccinimide.² We found it more convenient to react the 3-bromomethyl-2-nitrothiophen with pyridine, treat the product (12) with *NN*-dimethyl-4-nitrosoaniline, and

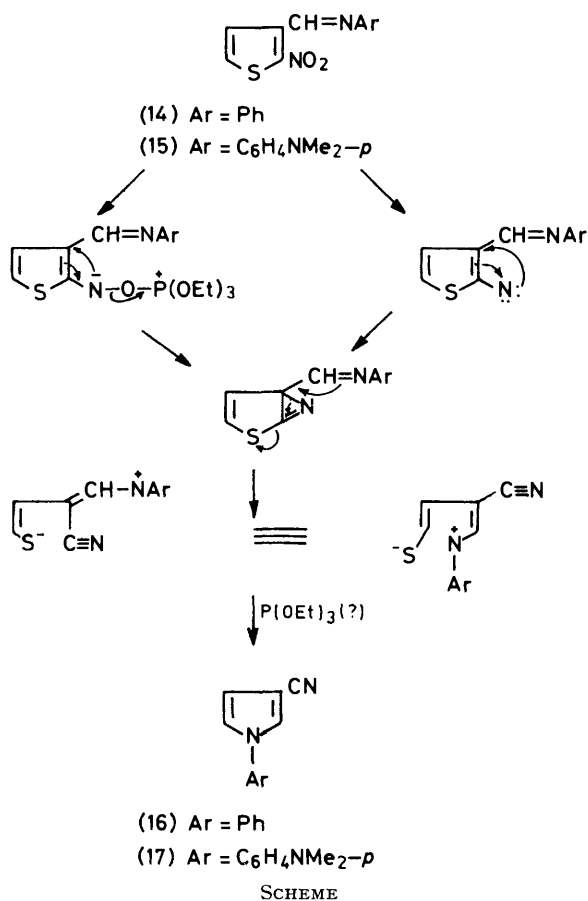


hydrolyse the nitrone (13) produced⁷ with 3*M*-sulphuric acid.

The ¹H n.m.r. spectra of 2-nitrothiophen-3-carbaldehyde and its isomer (measured in CDCl₃) are super-

impossible and consist of two singlets, one at $\tau -0.8$ for the aldehyde protons, and one at $\tau 2.25$ for 4- and 5-H which are accidentally equivalent. Complexation of the aldehyde group in 2-nitrothiophen-3-carbaldehyde with the shift reagent, $\text{Eu}(\text{fod})_3$,* allowed 4- and 5-H to be distinguished in this case.

Condensation of 3-methyl-2-nitrothiophen with *NN*-dimethyl-4-nitrosoaniline and treatment of the product with concentrated hydrochloric acid gave mainly starting material, together with a trace only of 2-nitrothiophen-3-carbaldehyde.



Condensation of 2-nitrothiophen-3-carbaldehyde with aniline and 4-dimethylaminoaniline gave anils (14) and (15), respectively.

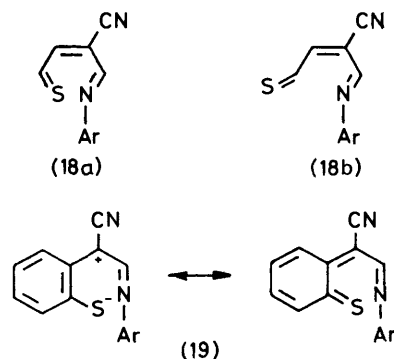
By contrast with the conversion of anils (1) and (2) into the corresponding thieno[3,2-*c*]pyrazoles (6) and (7) with triethyl phosphite and similar conversions reported previously,⁵ when the parent anil (14) in this series was treated with the same reagent in *t*-butylbenzene (ratio 1 : 3), it gave 1-phenylpyrrole-3-carbonitrile (16) as the major isolable product, as an unstable yellow oil. That the expected 5-phenylthieno[2,3-*c*]pyrazole was present in the mixture obtained as a yellow oil by distillation of the crude mixture was shown by mass spectrometry, but it was not isolated. The structure of the pyrrole (16)

* $\text{Eu}(\text{fod})_3$ is tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium.

followed from its spectroscopic analysis (see Experimental section), from its unambiguous synthesis by decarboxylation of the known⁸ 3-cyano-1-phenylpyrrole-2-carboxylic acid with copper in quinoline, and from its hydrolysis to the known⁸ 1-phenylpyrrole-3-carboxylic acid. Treatment of the anil (15) with triethyl phosphite in *t*-butylbenzene (1 : 3) similarly gave 1-(4-dimethylaminophenyl)pyrrole-3-carbonitrile (17) as the major isolable product. Following its purification by sublimation this compound appears to be extremely unstable in air, turning from white to pale blue crystals; it was identified by its spectroscopic properties. Although it is stable under nitrogen it was not possible to obtain a satisfactory elemental analysis. These thiophen \rightarrow pyrrole transformations can be rationalised by the mechanism shown in the Scheme, which is similar to that proposed previously⁵ in the benzo[*b*]thiophen area.

In the light of the preceding results we re-examined the reaction of anil (10; Ar = Ph) with triethyl phosphite, but using *t*-butylbenzene as a solvent (ratio 1 : 3) and employing a different work-up technique. This gave increased yields of the same products,⁵ namely 2-phenyl-[1]benzothieno[2,3-*c*]pyrazole (36% yield) and benzo[*b*]thiophen-3-carbonitrile (54%), thus confirming our earlier result.

The reasons for the difference in behaviour between anils (14) and (15) and anil (10) are not clear. A referee has suggested that the benzene ring in intermediate (19), may restrict internal rotation into a less hindered conformation analogous to (18b) which is possible for the other intermediate. Whatever the reason, intermediate (19) cyclises before desulphurisation can occur, whereas the opposite is the case with (18). It has not been possible to determine the fate of the sulphur. However, triethyl phosphite is known to be a good reagent for desulphurisation.



EXPERIMENTAL

General comments (spectroscopic instruments used, *etc.*) are the same as those given in Part 20.¹ ¹H N.m.r. and other spectroscopic data not given here are included in a Supplementary Publication.†

Light petroleum had b.p. 60–80 °C unless stated otherwise. The following compounds were prepared by literature

† Supplementary Publication No. SUP 22443 (3 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1978, Index issue.

procedures: 2-methyl-3-nitrothiophen (82%), m.p. 44–45 °C (from ethanol–light petroleum) (lit.,³ 44–45.5 °C) by dechlorosulphonation of 5-methyl-4-nitrothiophen-2-sulphonyl chloride;³ 3-methyl-2-nitrothiophen (50%), m.p. 62–63 °C (from ethanol–light petroleum) (lit.,⁶ 63 °C); 3-bromomethyl-2-nitrothiophen (64%), m.p. 63–64 °C (from light petroleum) (lit.,² 63–65 °C); and 3-cyano-1-phenylpyrrole-2-carboxylic acid, m.p. 198–200 °C (from chloroform–hexane) (lit.,⁸ 194–195 °C), ν_{\max} (Nujol) 1 680 (C=O), 2 230 (CN), and 2 400–3 300 cm^{-1} (OH).

N-(2-Nitro-3-thenyl)pyridinium Bromide (12).—A stirred mixture of 3-bromomethyl-2-nitrothiophen (2.85 g, 12.8 mmol), dry pyridine (1.19 g, 15.06 mmol), and dry ethanol (10 ml) was heated under reflux for 45 min, then allowed to cool to 0 °C overnight, and the product (3.84 g, 99%) filtered off, m.p. 232–233 °C (decomp.) (from ethanol) (lit.,² 232–233 °C).

Condensation of 2-Methyl-3-nitrothiophen with NN-Dimethyl-4-nitrosoaniline.—A solution of the nitroso-compound (2.25 g, 15.0 mmol) in ethanol (5 ml) was added dropwise to a stirred solution of 2-methyl-3-nitrothiophen (1.43 g, 10.0 mmol) in ethanol (5 ml) heated under reflux. Then pyrrolidine (10 drops) was added, the mixture was heated for a further 5 h, and then left overnight to cool to ambient temperature. The precipitate (1.7 g) was filtered off, dried, and shown by t.l.c. and ¹H n.m.r. and mass spectroscopy to be a mixture of *N*-(3-nitrothiophen-2-ylidene)-4-dimethylaminoaniline (2) (16 mol %) and its *N*-oxide (5) (84 mol %). The ratio of these two compounds in the mixture was determined by ¹H n.m.r. spectroscopy (integration of $-\text{CH}_2\text{N}^-$ protons); the chemical shifts for the anil (2) and its R_F value on t.l.c. were the same as those recorded using an authentic sample (see later). The product was stirred for 10 min at ambient temperature with 3*M*-sulphuric acid (25 ml) and poured on crushed ice. Extraction with ether gave *N*-(3-nitrothiophen-2-ylidene)-4-dimethylaminoaniline *N*-oxide (5) (0.98 g, 34%), m.p. 229–230 °C (from toluene) (Found: C, 53.7; H, 4.4; N, 14.3%; M^+ , 291.0682. $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$ requires C, 53.6; H, 4.5; N, 14.4%; M , 291.0678).

3-Nitrothiophen-2-carbaldehyde.—A mixture (0.5 g) of the anil (2) and the nitrone (5), prepared as described in the preceding experiment, was added to concentrated hydrochloric acid (10 ml). After heating the resulting mixture under reflux for 1 h, it was cooled, and extraction with ether gave 3-nitrothiophen-2-carbaldehyde (0.27 g), b.p. 122 °C at 0.08 mmHg (Kugelrohr apparatus) (lit.,² 113–127 °C at 2–3 mmHg), m.p. 54–55 °C (from ethanol–light petroleum), ν_{\max} 1 670 cm^{-1} (C=O).

N-(3-Nitrothiophen-2-ylidene)anilines.—*General method.* A mixture of 3-nitrothiophen-2-carbaldehyde (0.79 g, 5 mmol), the appropriate aromatic amine (5.5 mmol), and ethanol (10 ml) was stirred and heated under reflux for 10 min, then cooled to ambient temperature overnight. The precipitate was filtered off, washed with cold (0 °C) ethanol, and recrystallised. The following compounds were prepared: *N*-(3-nitrothiophen-2-ylidene)aniline (1) (86%), m.p. 59–60 °C (from light petroleum) (Found: C, 56.4; H, 3.5; N, 11.9. $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2\text{S}$ requires C, 56.9; H, 3.5; N, 12.0%); *N*-(3-nitrothiophen-2-ylidene)-4-dimethylaminoaniline (2) (90%), m.p. 164–165 °C (from ethanol) (Found: C, 56.5; H, 4.8; N, 15.3. $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$ requires C, 56.7; H, 4.8; N, 15.3%); *N*-(3-nitrothiophen-2-ylidene)-4-methylaniline (3) (94%), m.p. 97.5–98.5 °C (from light petroleum) (Found: C, 58.6; H, 4.0; N, 11.4. $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ requires

C, 58.5; H, 4.1; N, 11.4%); and *N*-(3-nitrothiophen-2-ylidene)-4-chloroaniline (4) (67%), m.p. 124–125 °C (from light petroleum) (Found: C, 49.3; H, 2.6; N, 10.65. $\text{C}_{11}\text{H}_7\text{ClN}_2\text{O}_2\text{S}$ requires C, 49.5; H, 2.65; N, 10.5%) (mass spectra were consistent with the structures assigned).

Reaction of N-(3-Nitrothiophen-2-ylidene)anilines with Triethyl Phosphite.—(a) A mixture of *N*-(3-nitrothiophen-2-ylidene)aniline (1) (0.70 g, 3.0 mmol), triethyl phosphite (1.50 g, 9.0 mmol), and *t*-butylbenzene (10 ml) was heated under reflux under nitrogen for 14 h. The solvent, the excess of reagent, and the triethyl phosphate produced were distilled off at 10^{-3} mmHg and the residue distilled slowly at 120 °C and 10^{-3} mmHg (Kugelrohr apparatus) to give an oily, yellow solid. This was fractionally recrystallised from light petroleum to give 5-phenylthieno[3,2-*c*]pyrazole (6) (0.09 g, 15%), crystals, m.p. 98–99 °C (from light petroleum), $\tau(\text{CDCl}_3)$ 1.95 (1 H, s, 6-H) and 2.10–3.00 (7 H, m, aromatic) (Found: C, 66.0; H, 4.1; N, 13.9%; M^+ 200. $\text{C}_{11}\text{H}_8\text{N}_2\text{S}$ requires C, 66.0; H, 4.0; N, 14.0%; M , 200), and diethyl *N*-(2-*N*-phenylthienylidene)phosphoramidate (8) (0.16 g, 16%), yellow crystals, m.p. 80.5–81 °C (from light petroleum), ν_{\max} (Nujol) 3 150 (NH) and 1 605 cm^{-1} (C=N), $\tau(\text{CDCl}_3)$ 1.53 (1 H, s, CH_2N), 2.52–2.96 (7 H, m, aromatic), 5.85 (4 H, q, J 7.5 Hz, CH_2), and 8.66 (6 H, t, J 7.5 Hz, Me) (Found: M^+ , 338.0856. $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_3\text{PS}$ requires M , 338.0854). The parent molecular ion underwent two successive losses of fragments with m/e 28 (ethylene) and subsequent loss of H_2O ; the corresponding metastables were present.

(b) A mixture of *N*-(3-nitrothiophen-2-ylidene)-4-dimethylaminoaniline (0.825 g, 3.0 mmol), triethyl phosphite (1.50 g, 9.0 mmol), and *t*-butylbenzene (10 ml) was heated under reflux under nitrogen for 16 h, then left to cool overnight to ambient temperature. A yellow solid (0.22 g) was filtered off. The excess of reagent, the solvent, and the triethyl phosphate produced were distilled off under reduced pressure and careful distillation of the residue at 120 °C and 10^{-3} mmHg (Kugelrohr apparatus) gave a further amount (0.1 g) of the yellow solid. The two fractions were combined and recrystallised from toluene to give 5-(4-dimethylaminophenyl)thieno[3,2-*c*]pyrazole (7) (0.20 g, 27%), m.p. 169–170 °C, $\tau(\text{CDCl}_3)$ 2.07 (1 H, s, 6-H), 2.40 and 3.27 (4 H, 2 × d, J 8.75 Hz, aromatic), 2.64 and 2.87 (2 H, 2 × d, J 5.0 Hz, 2- and 3-H), and 7.00 (6 H, s, NMe_2) (Found: C, 64.0; H, 5.35; N, 17.2%; M^+ , 243. $\text{C}_{13}\text{H}_{13}\text{N}_3\text{S}$ requires C, 64.2; H, 5.4; N, 17.3%; M , 243).

N-(2-Nitrothiophen-3-ylidene)-4-dimethylaminoaniline *N*-Oxide (13).—A mixture of *N*-(2-nitro-3-thenyl)pyridinium bromide (12) (0.33 g, 1.1 mmol), *NN*-dimethyl-4-nitrosoaniline (0.15 g, 1.0 mmol), and ethanol (15 ml) was stirred for 10 min at –20 °C, then warmed to 0 °C, when 1*M*-sodium hydroxide (1.81 ml) was added dropwise during 5 min. The mixture changed colour from dark green to red. Stirring was continued for a further 45 min and the product (13) (0.24 g, 75%) was filtered off, deep red solid, m.p. 169–170 °C (from toluene) (Found: C, 54.1; H, 4.7; N, 14.3%; M^+ , 291. $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$ requires C, 53.6; H, 4.5; N, 14.4%; M , 291).

2-Nitrothiophen-3-carbaldehyde.—A mixture of the nitrone (13) (5.14 g, 17.66 mmol) and 3*M*-sulphuric acid (588 ml) was stirred for 10 min at ambient temperature, then poured on crushed ice. Extraction with ether gave the aldehyde (2.7 g, 97%), b.p. 95–100 °C at 5×10^{-3} mmHg (Kugelrohr apparatus), m.p. 55–56 °C (from ether–light petroleum) (lit.,² 55.6–56.5 °C), ν_{\max} (Nujol) 1 680 cm^{-1} (C=O).

N-(2-Nitrothiophen-3-ylidene)aniline (14) (89%), orange crystals, m.p. 75–76 °C (from ethanol), ν_{\max} (Nujol) 1 595 cm^{-1} (C:N) (Found: C, 56.8; H, 3.5; N, 12.1%; M^+ , 232. $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2\text{S}$ requires C, 56.9; H, 3.5; N, 12.1%; M , 232), and N-(2-nitrothiophen-3-ylidene)-4-dimethylaminoaniline (15) (91%), m.p. 175–176 °C (from ethanol), ν_{\max} (Nujol) 1 615 cm^{-1} (C:N) (Found: C, 56.65; H, 4.8; N, 15.4%; M^+ , 275. $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$ requires C, 56.7; H, 4.8; N, 15.3%; M , 275), were prepared by the general method described before for anils (1)–(4). Freshly distilled aniline and 4-dimethylaminoaniline were essential to obtain the yields quoted.

Reaction of N-(2-Nitrothiophen-3-ylidene)aniline (14) with Triethyl Phosphite.—(a) A mixture of the anil (14) (0.70 g, 3.0 mmol), triethyl phosphite (1.90 g, 11.0 mmol), and *t*-butylbenzene (10 ml) was heated under reflux under nitrogen for 14 h. The mixture was heated gradually to 200 °C under reduced pressure (10^{-3} mmHg); the last, yellow fraction (0.39 g) was chromatographed on alumina. Ether eluted 1-phenylpyrrole-3-carbonitrile (16) (0.28 g, 55%), b.p. 105 °C at 5×10^{-3} mmHg (Kugelrohr apparatus), ν_{\max} (Nujol) 3 165 (pyrrole CH) and 2 255 cm^{-1} (CN), $\tau(\text{CDCl}_3)$ 2.40–3.50 (6 H, m, 2-H and C_6H_5), 3.03 (1 H, m, 5-H), and 3.48 (1 H, m, 4-H) (Found: M^+ , 168.0692. $\text{C}_{11}\text{H}_8\text{N}_2$ requires M , 168.0687).

(b) The preceding experiment was repeated using anil (1.3 g). *t*-Butylbenzene was distilled off under reduced pressure, the residue was dissolved in ether, the ethereal solution was dried (MgSO_4), and distillation gave triethyl phosphite followed by 1-phenylpyrrole-3-carbonitrile (0.83 g, 88%), identical (b.p., i.r., and n.m.r. spectra) with other samples.

Hydrolysis of 1-Phenylpyrrole-3-carbonitrile.—A mixture of the nitrile (0.20 g, 1.19 mmol) and 10% aqueous sodium hydroxide (3 ml) was heated under reflux for 2 h. Because the nitrile was insoluble and reacted only slowly, ethanol (1 ml) was added, and the mixture heated under reflux for a further 17 h. The mixture was acidified, the crude product was filtered off, dissolved in ether (25 ml), and the ethereal solution was extracted with 20% aqueous sodium hydroxide. The basic extracts were combined, acidified, and the product was filtered off, dried, and recrystallised from light petroleum–chloroform to give 1-phenylpyrrole-3-carboxylic acid (0.18 g, 79%), m.p. 118–119 °C (lit.,⁸ 119–120 °C), ν_{\max} (Nujol) 1 670 cm^{-1} (C:O); $\tau(\text{CDCl}_3)$ 0.7–1.3br (1 H, s, OH), 2.2 (1 H, m, aromatic), 2.6 (5 H, s, aromatic), 3.0 (1 H, m, aromatic), and 3.2 (1 H, m, aromatic).

Reaction of N-(2-Nitrothiophen-3-ylidene)-4-dimethylaminoaniline with Triethyl Phosphite.—A mixture of the anil (15) (0.45 g, 1.6 mmol), triethyl phosphite (0.89 g, 5.4 mmol), and *t*-butylbenzene (8 ml) was heated under reflux under nitrogen for 14 h, then left to cool to ambient temperature overnight. The precipitate (0.17 g) was filtered off and the filtrate distilled at 25 °C and 5×10^{-2} mmHg. The last fraction was a pale blue solid (0.073 g), identical (i.r.) with

the precipitate. The two solids were combined (0.24 g, 70% crude) and recrystallised from toluene–light petroleum to give 1-(4-dimethylaminophenyl)pyrrole-3-carbonitrile (17), m.p. 150–151 °C (sublimed at 65–69 °C and 7×10^{-3} mmHg), white crystals which became blue immediately on exposure to the air, ν_{\max} (Nujol) 3 165 (pyrrole CH) and 2 255 cm^{-1} (CN), $\tau(\text{CDCl}_3)$ 2.60 (1 H, m, 2-H), 2.79 and 3.25 (4 H, 2 \times d, J 9.0 Hz, C_6H_4), 3.09 (1 H, m, 5-H), 3.45 (1 H, m, 4-H), and 6.99 (6 H, s, NMe_2) (Found: M^+ , 211.1104. $\text{C}_{13}\text{H}_{13}\text{N}_3$ requires M , 211.1109) (see Discussion section for comment).

1-Phenylpyrrole-3-carbonitrile (16).—A mixture of 3-cyano-1-phenylpyrrole-2-carboxylic acid (0.2 g, 0.94 mmol), copper bronze powder (0.05 g, 0.79 mg atom), and redistilled quinoline (4 ml) was heated under reflux for 1.75 h, then cooled, and added to ether (50 ml). The ethereal solution was washed successively with 1M-hydrochloric acid (3×100 ml), 10% aqueous sodium hydrogencarbonate (2×50 ml), and water (3×100 ml), and dried (MgSO_4). Distillation gave 1-phenylpyrrole-3-carbonitrile (0.105 g, 66%), b.p. 105 °C at 3×10^{-4} mmHg, identical (i.r., ^1H n.m.r., and mass spectra and t.l.c. R_F values) with the sample prepared as described before.

Reaction of N-(2-Nitrobenzo[b]thiophen-3-ylidene)-4-dimethylaminoaniline with Triethyl Phosphite.—A mixture of the anil (0.15 g, 0.46 mmol), triethyl phosphite (0.27 g, 1.6 mmol), and *t*-butylbenzene (5 ml) was heated under reflux under nitrogen for 14 h. Distillation at 5×10^{-3} mmHg (Kugelrohr apparatus) with gradual heating to 160 °C gave a solid (0.086 g) which was recrystallised from light petroleum to yield benzo[b]thiophen-3-carbonitrile (0.04 g, 54%), m.p. 68–70 °C (from light petroleum) (lit.,⁵ 69–71 °C). Distillation was continued and, at 170–175 °C, gave a yellow liquid which solidified as 2-phenyl[1]benzothieno[2,3-*c*]pyrazole (0.05 g, 36%), m.p. 113–115 °C (from light petroleum) (lit.,⁵ 115–117 °C).

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