

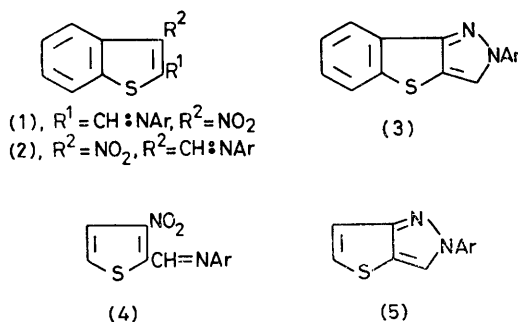
## Novel Ring Transformation of a Thiophen into a Pyrrole<sup>1</sup>

By VERONICA M. COLBURN, BRIAN IDDON,\* HANS SUSCHITZKY, and (in part) PETER T. GALLAGHER

(The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford, Lancashire M5 4WT)

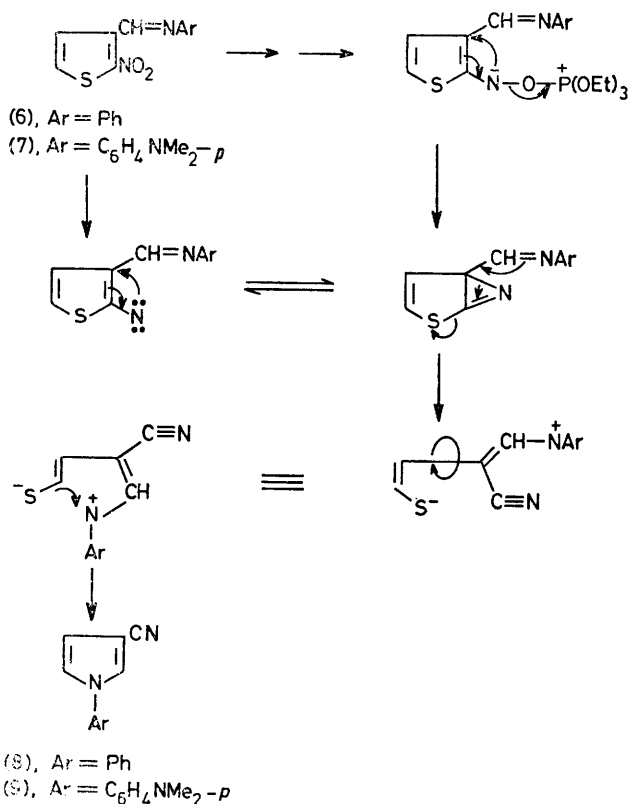
**Summary** Whereas anils (4) derived from 3-nitrothiophen-2-carbaldehyde undergo reductive cyclisation with triethyl phosphite to give the expected 2-arylthieno[3,2-*c*]pyrazoles (5), the isomeric anils (6) and (7), derived from 2-nitrothiophen-3-carbaldehyde, give the 1-arylpyrrole-3-carbonitriles (8) and (9), respectively, as the major products.

REDUCTIVE cyclisation of anils with the general structure (1) with trivalent phosphorus reagents yields the corresponding 2-aryl[1]benzothieno[3,2-*c*]pyrazole (3).<sup>2</sup> By contrast, however, the isomeric anils (2) give mixtures of the corresponding benzothieno[2,3-*c*]pyrazole and benzo[*b*]thiophen-3-carbonitrile.<sup>2</sup> We have proposed a mechanism which accounts for the formation of the latter compound through an interesting ring-opening–ring-closure sequence of the thiophen ring. In the light of these results it was of interest to study the behaviour of the corresponding thiophen anils.



As expected, treatment of anils with the general structure (4) with triethyl phosphite in *t*-butylbenzene (1 : 3) gave the corresponding thieno[3,2-*c*]pyrazole (5).<sup>3</sup> Compound (6), however, after 14 h under these conditions gave 1-phenylpyrrole-3-carbonitrile (8) as the major product (55% yield), isolated by successive distillation (10<sup>-3</sup> mmHg) and chromatography on alumina, b.p. 105 °C at 5 × 10<sup>-3</sup> mmHg (Kugelrohr apparatus);  $\nu_{\max}$  2255 cm<sup>-1</sup> (CN);  $\tau$  (CDCl<sub>3</sub>) 2.40–3.50 (6H, m, Ph and 2-H), 3.03 (1H, m, 5-H), and 3.48 (1H, m, 4-H);  $m/e$  168.0692 ( $M^+$ ). This compound was an unstable, yellow oil and it was not possible to obtain a satisfactory elemental analysis, although the values obtained were close to those expected. However, compound (8) was synthesised unambiguously from the known<sup>4</sup> ethyl 3-cyano-1-phenylpyrrole-2-carboxylate by hydrolysis to the corresponding acid, m.p. 198–200 °C (from hexane-chloroform) (lit.<sup>4</sup> 194–195 °C);  $\nu_{\max}$  (Nujol) 3300–2400br (OH), 2230 (CN), and 1680 cm<sup>-1</sup> (CO), and decarboxylation

of the acid (in 66% yield) with copper in quinoline. Reductive cyclisation of the anil (7) with triethyl phosphite in *t*-butylbenzene likewise gave 1-(4-dimethylaminophenyl)pyrrole-3-carbonitrile (70% crude), m.p. 150–151 °C (sublimed at 65–69 °C and 7 × 10<sup>-3</sup> mmHg);  $\nu_{\max}$  2255 cm<sup>-1</sup> (CN);  $\tau$  (CDCl<sub>3</sub>) 2.60 (1H, m, 2-H), 2.79 and 3.25 (4H, 2 × d,  $J$  9.0 Hz, ArH), 3.09 (1H, m, 5-H), 3.45 (1H, m, 4-H), and 6.99 (6H, s, NMe<sub>2</sub>);  $m/e$  211.1104 ( $M^+$ ). This compound sublimed as white crystals which turned pale blue immediately on exposure to air.



SCHEME

A mechanism which accounts for our observations is shown in the Scheme; the formation of the bicyclic intermediate and the ring-opening steps are analogous to those given in our earlier, related communication.<sup>2</sup> Possible reasons for the difference in behaviour of anils (2) and (6) will be examined in the full paper later.

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<sup>1</sup> See H. C. Van Der Plas, 'Ring Transformations of Heterocycles,' Vol. 1, Academic Press, London and New York, 1973, ch. 3, p. 198.

<sup>2</sup> K. E. Chippendale, B. Iddon, and H. Suschitzky, *J.C.S. Perkin I*, 1973, 129.

<sup>3</sup> V. M. Colburn, B. Iddon, and H. Suschitzky, unpublished results.

<sup>4</sup> R. Huisgen and E. Lashtuvka, *Chem. Ber.*, 1960, 93, 65.