New Unusual Synthesis of *N*-Arylpyrroles

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Summary Thermolysis of mono *N*-(4-arylsulphenylbut-2-ynyl)anilines affords an unusual synthesis of *N*-arylpyrroles.

WE here report a new synthesis of *N*-arylpyrroles by the thermal rearrangement of mono *N*-(4-arylsulphenylbut-2-ynyl)anilines (**1**). The starting materials (**1**) for the rearrangement were obtained in good yields (30—70%) from the reaction of 1-chloro-4-arylsulphenylbut-2-ynes[1] with the appropriate anilines in refluxing aqueous tetrahydrofuran.

$$p\text{-}RC_6H_4\cdot S\cdot CH_2C\equiv CCH_2Cl + H_2N\cdot C_6H_4Me\text{-}p$$
$$\downarrow$$
$$p\text{-}RC_6H_4\cdot S\cdot CH_2C\equiv CCH_2NHC_6H_4Me\text{-}p$$

(**1**)

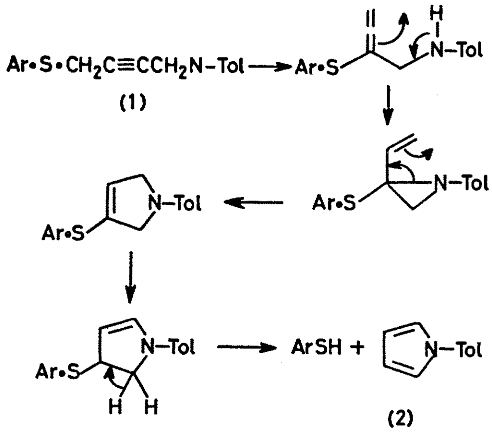
a; R = Me, m.p. 49 °C.
b; R = Cl, m.p. 61 °C

The solid products were purified by recrystallization from CH_2Cl_2–light petroleum. Excellent elemental analyses and n.m.r. and mass spectra supported the structures assigned.

A solution of the anilinosulphide (**1a**) in ethylene glycol was refluxed vigorously under nitrogen for 4 days. The product sublimed directly on to the condenser giving a 36% yield of the pyrrole (**2**). The melting point and n.m.r. and mass spectra of (**2**) were identical to those reported.[2]

The elimination of the benzenethiol unit and the formation of *N*-(*p*-tolyl)pyrrole (**2**) was confirmed by the similar reaction of (**1b**). The reaction was allowed to proceed under a steady stream of nitrogen in a vessel equipped with a dry ice condenser on top of a water condenser. The eliminated *p*-chlorobenzenethiol was deposited on the dry ice condenser as needles while the pyrrole was deposited on the water condenser as colourless plates. The pyrrole obtained from (**1b**) was identical with that formed from (**1a**).

The elimination of the benzenethiol unit in such a ready fashion excludes the possibility of a thio Claisen rearrangement. Alternatively, a 1,3-migration of the arylsulphenyl function[3] could lead to the sequence of transformations in the Scheme. The 1,5-hydrogen abstraction by the allene



a; Ar = p-MeC$_6$H$_4$
b; Ar = p-ClC$_6$H$_4$
SCHEME. Tol = p-MeC$_6$H$_4$

has ample analogies in several abnormal Claisen rearrangements.[4] The ready ring expansion of vinyl aziridines to pyrroles has also been noted earlier.[5] Subsequent elimination of benzenethiol[6] from the aryl allyl sulphide is frequently encountered.

The unusual transformation of an *N*-(but-2-ynyl)aniline into an *N*-arylpyrrole appears to be unique and is significantly different from known pyrrole syntheses.[7]

We thank the Robert A. Welch Foundation for a graduate Fellowship (P. E. G.) and the funds for support of this work.

(*Received, 9th January* 1979; *Com.* 024.)

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