Reaction of Pyrrolylmagnesium Bromide with Toluene-*p*-sulphonyl Azide

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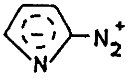
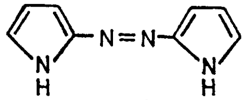
Summary The reaction of pyrrolylmagnesium bromide with toluene-*p*-sulphonyl azide affords 2,2′-azopyrrole, indicating that the reaction takes place *via* a diazopyrrole intermediate

ALTHOUGH diazocyclopentadiene has been synthesized by the reaction of lithium cyclopentadienide with toluene-*p*-sulphonyl azide,[1] its heterocyclic analogue, diazopyrrole (**1**), has not been obtained by the similar reaction of pyrrol-1-yl-lithium [2] The reaction of pyrrol-1-ylmagnesium



(1)



(2)

bromide[3] with toluene-*p*-sulphonyl azide in ether under reflux gave 2,2′-azopyrrole (**2**) as orange needles (15%), m.p. 155·0—155·5° (decomp.); i.r. (KBr) 3260 cm^{-1} (N–H stretch); u.v. (cyclohexane) λ_{max} 293 (ϵ 2800), 412 (34,200), and 429 (34,000) nm.

In the n.m.r. spectrum of (**2**) [$(CD_3)_2SO$] the broad singlet at τ −1·5 (1H) is assigned to N–*H* since it disappears on addition of D_2O. Three multiplets of equal area (1H) centred at τ 3·35, 3·73, and 3·10 are assigned to 3-, 4-, and 5-H, respectively, by analogy with the spectra of pyrrole derivatives substituted at the 2-position by CHO, COMe, and CN.[4] In all these spectra, the signals from protons adjacent to the substituents are strongly shifted to lower field by 0·48—0·76 p.p.m. than in unsubstituted pyrrole, whereas the protons in the other positions are relatively less affected. Thus, (**2**) is confirmed to the 2,2′- and not the 3,3′- isomer.

The formation of (**2**) is strong evidence that (**1**) is formed in the reaction. It is known that aromatic diazonium compounds react with Grignard reagent, to afford azo-compounds.[5] Pyrrol-1-ylmagnesium bromide may be more effective in this synthesis than pyrrol-1-yl-lithium because of the difference in the ionic nature of the N–Mg and N–Li bonds. Thus, pyrrol-1-ylmagnesium bromide reacts with toluene-*p*-sulphonyl azide at the 2-position to yield (**1**) which further reacts to give (**2**), but a similar reaction of 1-pyrrol-1-yl-lithium would occur predominantly at the 1-position to give an unstable aminoazo-compound.

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