Cycloadditions of α-Aminonitrile Diene
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Cycloadditions of 2-(N-methylanilino)hexa-2,4-dienenitrile with the dienophiles maleic anhydride, N-phenylmaleimide, benzoquinone, or dimethyl acetylenedicarboxylate led to methyldiarylamines after loss of hydrogen cyanide and oxidative aromatisation.

α-Dialkylaminonitriles have been extensively used as nucleophilic acyl equivalents,1 and α-methyleneaminonitriles as Michael acceptors,2,3 but the corresponding α-aminoedienenitriles have not yet been investigated. We herein report the cycloadditions of the α-amino-hexadienenitrile (1), and demonstrate that its α-carbon atom functions as an electrophilic centre.

According to the Peterson procedure,2 treatment of N-methylanilinoacetonitrile consecutively with lithium diisopropylamide (LDA), Me3SiCl, LDA, and crotonaldehyde afforded a 1:1 mixture of the dienes (1a) and (1b) in 78% yield. The isomers were separated by flash chromatography (ethyl acetate-hexane, 1:19), and their structures determined by n.m.r. spectroscopy. The large value of J(4-H75-H) [14.8 Hz for (1a) and 15.2 Hz for (1b); 400 MHz 1H n.m.r.] shows that the 4,5-double bond has the E-configuration in both dienes, but the configuration of the 2,3-double bonds differs. Compound (1a) (Rf 0.37) has the 2E configuration, the 3-H resonance appearing at δ 6.25 (d, J 11 Hz), while the 3-H resonance in the 2Z isomer (1b) appears at lower field (δ 6.63) owing to the deshielding effect of the cyano group.4,5 The reaction of the diene (1a) and maleic anhydride (1.2 equiv.) in refluxing xylene for 24 h gave a single product (2) in 80% yield after purification by flash chromatography, m.p. 126—128 °C, λmax (CHCl3) 432, 324, 300, and 252 nm. It showed no cyano i.r. absorption at ~2220 cm−1, and its 1H n.m.r. spectrum showed seven aromatic protons (δ 6.90—7.40) and two singlets at δ 3.48 (N-Me) and 2.63 (Ar-Me). Its 13C n.m.r. spectrum was also compatible with structure (2) [2 × Me, δ 17.1 and 41.5; 2 × C=O, δ 160.5 and 163.2; 12 Ar-C]. Structure (2) was confirmed by elemental analysis and mass spectroscopy (M+, m/z 267). The reaction of the diene (1b) and maleic anhydride similarly gave the diarylamine (2) (80% yield) after reflux for 30 h, and the reaction of a 1:1 mixture of the dienes (1a) and (1b) with maleic anhydride showed that the dienes were consumed at a similar rate. Although the
The mechanism of this reaction is not clear since intermediates could not be isolated, we assume that it involves a dipolar process (Scheme 1), as usually encountered in enamine systems. Since the cycloaddition was performed at an elevated temperature, HCN would be easily eliminated and subsequent oxidative aromatisation would afford the observed product. We surmise the oxidation possibly occurred during work-up (removal of xylene in vacuo) or chromatography.

The cycloadducts (3), (4), and (5) were similarly formed in 75, 67, and 40% yields, respectively, when the diene (1) was heated with N-phenylmaleimide, benzoquinone (1:1 adduct), and dimethyl acetylenedicarboxylate in refluxing xylene or decalin. Since the nitrogen atom and the aromatic moiety of dienes (1) are readily further functionalised, this method is potentially synthetically versatile. We are currently investigating reaction with other α-aminonitrile dienes and the transformation of the cycloadducts (2)—(5) to acridones.

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References

† All compounds had satisfactory elemental analysis and spectroscopic properties (u.v., i.r., electron impact mass spectrum, 1H and 13C n.m.r.), except that the 13C n.m.r. spectrum of compound (5) was not recorded.