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 -aminodienenitriles 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-H,5-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) (R_f 0.37) has the 2*E* 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, $\lambda_{max.}$ (CHCl₃) 432, 324, 300, and 252 nm. It showed no evano 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) $[2 \times Me, \delta]$ 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



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.⁶ Since the cycloaddition was performed at an elevated temperature, HCN would be easily eliminated⁷ 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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[†] 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.