Cycloadditions of α-Aminonitrile Diene

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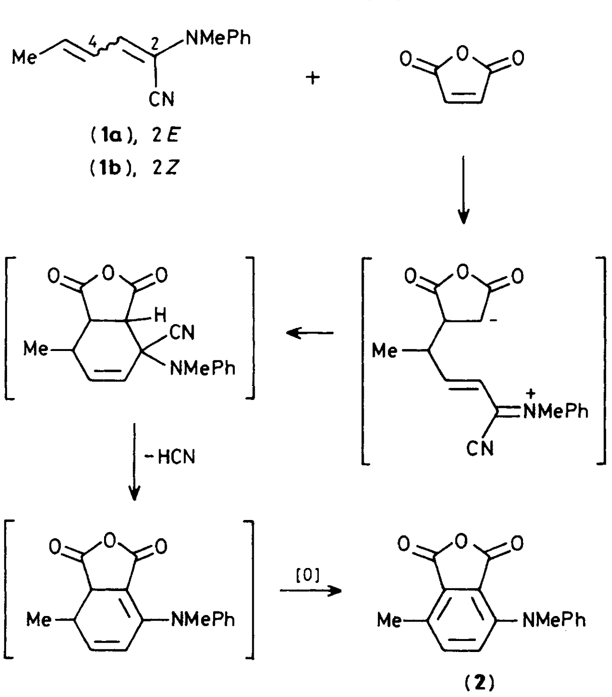
Cycloadditions of 2-(*N*-methylanilino)hexa-2,4-dienenitrile with the dienophiles maleic anhydride, *N*-phenylmaleimide, benzoquinone, or dimethyl acetylenedicarboxylate led to methyldiarylamines after loss of hydrogen cyanide and oxidative aromatisation.

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.

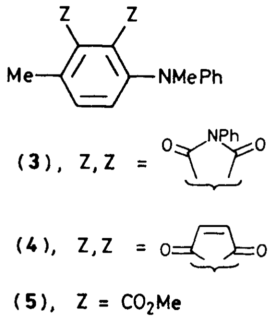
According to the Peterson procedure,[2] treatment of *N*-methylanilinoacetonitrile consecutively with lithium diisopropylamide (LDA), Me_3SiCl, LDA, and crotonaldehyde afforded a 1:1 mixture of the dienes (**1a**) and (**1b**) in 78% yield. The isomers were separated by flash chromatography (ethyl acetate–hexane, 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 ^{1}H 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 2*Z* 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, $\lambda_{max.}$ ($CHCl_3$) 432, 324, 300, and 252 nm. It showed no cyano i.r. absorption at ~2220 cm^{-1}, and its ^{1}H 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 ^{13}C 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



Scheme 1

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 eliminated[7] 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, ^{1}H and ^{13}C n.m.r.), except that the ^{13}C n.m.r. spectrum of compound (**5**) was not recorded.