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REACTIONS OF 1,1-BIS(N,N-DIMETHYLAMINO)-1,3-BUTADIENE WITH OLEFINS. ZWITTERION FORMATION AND (4+2) CYCLOADDITION AS COMPETING PATHWAYS.

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Reactions of 1,1 bis(N,N-dimethylamino)-1,3-butadiene (2) with acrylonitrile and tetracyanoethylene are described. At 80°C acrylonitrile affords a (4+2) cycloadduct (3), whereas a zwitterion (4), formed from 2 and tetracyanoethylene even at -40°C, is characterized in solution and trapped as picrate. It eliminates hydrogen cyanide at T>-20°C to give a cyanine (5). Ring closure of the zwitterion either to a (2+2) or to a (4+2) cycloaduct is not observed.

The factors which determine the concerted or stepwise nature of normal Diels-Alder reactions have to be known in order to predict possible mechanisms for cycloadditions of this type. Besides a concerted pathway biradical and zwitterionic intermediates have been proposed and it has become evident that the substitution pattern of the reactants plays an important role in this context.[1] The formation of a zwitterion was shown recently when a substituted tetrazine and a ketene aminal, typical components of a Diels-Alder addition with inverse electron demand, were reacted.[2] It has been demonstrated also that radical ions are formed when 1,4-bis(N,N-dimethylamino)-1,3-butadiene (1) reacts with dienophiles of strong electron acceptor capacity.[3] It was established that the cycloadducts, formed in these reactions, cannot be the result of a concerted process.

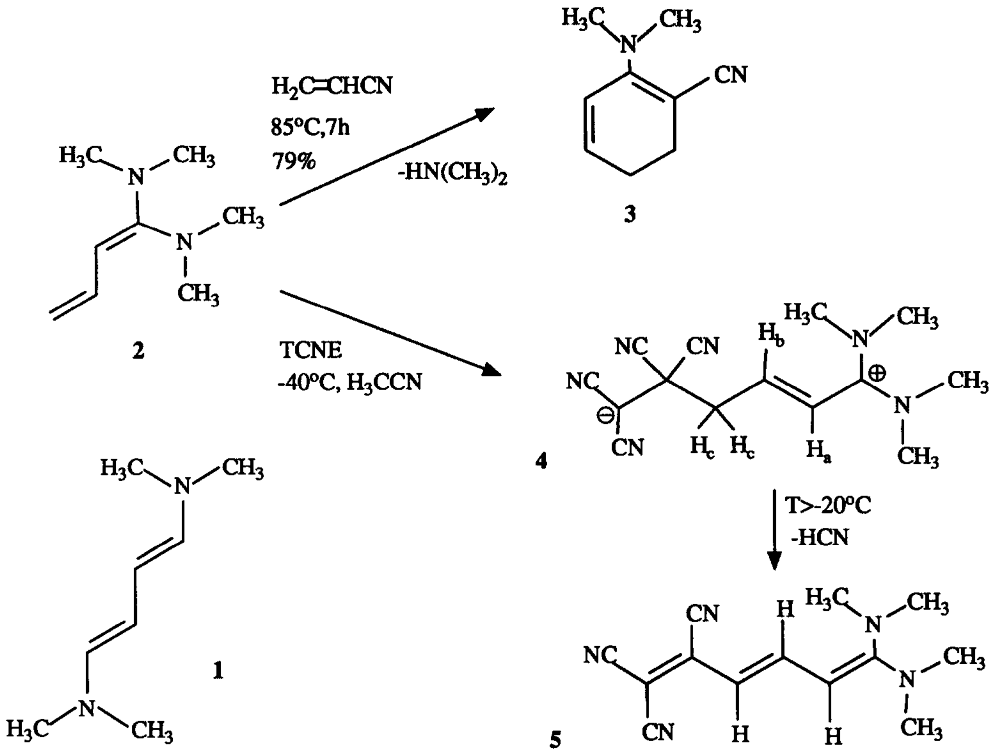
The studies on the symmetrical diene (1) have now been complemented by investigations on the corresponding unsymmetrically substituted diene (2) in order to compare it's reactivity with that of 1. 1,1-Disubstituted or cis-1-substituted dienes prefer strongly an anti-periplanar conformation and are influenced in their reactivity by the fact that a syn-periplanar conformation, necessary for a concerted (4+2) cycloaddition cannot be realized easily. This explains their normally reduced reactivity.[1,4] However, these and open-chain dienes in general offer the possibility that a reaction might start in the anti-periplanar conformation. This could result in other products than (4+2) cycloadducts.

The electron-rich character of 2[5] shows up in it's first vertical ionization potential (1. IP_v = 6.95 eV from the photoelectron spectrum) and the $E_{1/2}$ vs. SCE value (+0.03 V). Compared with 1 (1. IP_v = 6.46 eV, $E_{1/2}$= -0.33 V vs. SCE)[3] a slightly more positive value of the 1. IP and $E_{1/2}$ is observed, indicating reduced nucleophilic character for 2. A complete interpretation of the photoelectron spectrum shows that one of the dimethylamino groups must be in a perpendicular or almost perpendicular position relative to the plane of the π-system.[6] Cycloadditions of 2 have not been reported so far. Some reactions of a related system with a methyl group in 2-position of the diene system were carried out some time ago.[7] In that study a rather poor cycloaddition behavior was noticed.

The reaction of an equimolar solution (10% in each component) of **2** and acrylonitrile at 85°C in acetonitrile gave after 7 h 79% of **3**[8] which derives from the primary cycloadduct by elimination of dimethylamine. The reaction is slower in benzene under comparable conditions. No reaction is observed in benzene at room temperature within 6 d. If equimolar solutions of **2** and tetracyanoethylene are mixed in acetonitrile at -40°C a deeply blue coloured solution is formed immediately (broad absorption band with λ_{max}= 618 nm (ϵ= 40)) and no starting material can be detected by ^{1}H-NMR spectroscopy. Instead a ^{1}H NMR spectrum (CD_3CN) is observed which is in agreement with the presence of the zwitterion **4**. It displays signals for two olefinic protons at 6.27 (H_a) and 6.61 ppm (H_b) with J_{ab}= 17 Hz. Thus, an E-configuration of a double bond is established. A two proton signal is detected at 3.09 ppm (H_c) displaying a coupling of J_{bc}= 7.3 Hz with proton b. The twelve protons of the methyl groups appear as two signals for 6 protons each at 3.12 and 3.08 ppm. The chemical shift of the latter protons is close to that of the protons in the dimethylammonium ion (3.3 ppm)[9] and not to that of the protons in dimethylamine (2.3 ppm)[9]. Further support for the zwitterionic structure **4** comes from the ^{13}C NMR data. The signal at 167.1 ppm for a quartenary carbon is assigned to the carbon next to the two dimethylamino groups, carrying formally the positive charge.[10] The two olefinic carbons show signals at 143.3 and 126.7 ppm, the cyano group's carbon atoms appear at 125.0 and 116.9 ppm. The signal at 40.2 ppm stems from the methylene carbon, those at 37.6 and 20.1 ppm represent the carbon atoms with the cyano substituents. The signal at highest field (20.1 ppm) is due to the negatively charged carbon atom connected with two cyano groups. If picric acid is added at -40°C a crystalline picrate can be isolated in 64% which is fairly stable at room temperature and can be characterized by elemental analysis and spectroscopic techniques. [11] The experiments confirm that the zwitterion is generated from the anti-periplanar conformation of **2**.

The solution of **4** in acetonitrile is not stable above -20°C. The colour changes from blue slowly to deep red and is stable if the solution is warmed to room temperature. A red crystalline compound can be isolated in 90.5% yield with $mp_{dec.}$= 186 - 187°C. This compound is characterized by three ^{1}H-NMR signals (CD_3CN) for olefinic protons at 7.29 (1H, dd, ^3J= 12.0, ^4J= 0.8 Hz), at 6.26 ppm (1H, dd, ^3J= 12.0, ^4J= 0.8 Hz), and at 5.60 ppm (1H, d, ^3J= 14.4 Hz). A singlet is recorded for the 12 methyl protons at 3.08 ppm. The ^{13}C NMR data (d_6-acetone) with 6 signals for olefinic carbons at 170.3, 148.6, 128.1, 106.5, 43.8, and 42.6 ppm, together with signals at 42.9 (CH_3 of $N(CH_3)_2$), 115.3 and 113.3 for cyano carbon atoms indicate a highly polar structure. Together with the elemental analysis and the UV spectrum in acetonitrile, showing a strong absorption at λ = 489 nm (ϵ = 52053) , the results indicate structure **5** for the red compound. It is formed from the zwitterion by elimination of hydrogen cyanide and supports indirectly also the structure for the zwitterion. **3** constitutes the first characterized zwitterion from the reaction of an electron-rich diene and an electron-deficient olefin.

The results for the reaction of **2** with the two olefins can be interpreted as follows: Acrylonitrile as the less electron deficient system reacts at elevated temperatures with the syn-periplanar form of **2** which is in equilibrium with the anti-periplanar conformation at that temperature and gives a cycloadduct. It does not form a stable zwitterion because of insufficient stabilization of the negative charge by one cyano group. Whether this cycloaddition takes place via a zwitterionic pathway cannot be decided. It seems improbable that the dienophile attacks the anti-periplanar conformation of **2**. Tetracyanoethylene as a highly electron



deficient olefin is capable of reacting directly with the anti-periplanar conformation of **2** even at low temperature to give a zwitterion. Two cyano groups at the negative end provide enough stabilization to make the zwitterion persistent. Diene **2** does not need to undergo a conformational change to a syn-periplanar conformation prior to reaction. If the zwitterion were to form the (4+2) cycloadduct it would have to rotate about the CC double bond in the zwitterion. This is clearly not possible at -40°C. The zwitterion could in principle lead to a (2+2) cycloadduct, a substituted vinyl cyclobutane, without much conformational change. As is demonstrated by the experimental results the zwitterionic structure seems to be more stable in solution. Higher temperatures which might allow a conformational change to the structure for ring closure to a six-membered ring facilitate an elimination as competing reaction, thus preventing cycloadduct formation. It would be interesting to see whether a corresponding diene with a syn-periplanar fixed structure would also give a stable zwitterion, or whether it would prefer a ring closed structure.

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5. Barton, D. H. R., Hewitt, G., Sammes, P. G.; *J. Chem. Soc. (C)* **1969,** 16. The synthesis was slightly modified because the final product was still contaminated with an intermediate. By heating the product under argon at 80°C over calcium for three days pure **2** was obtained by condensation under vacuum.
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8. **3** is isolated after evaporation of the solvent by chromatography on neutral aluminumoxide with diethylether/n-pentane 1:1 as a yellow oil. It was characterized by elemental analysis and spectroscopic techniques. ^{13}C NMR ($CDCl_3$): $\delta = 22.6$ (CH_2), 25.7 (CH_2), 41.4 ($N(CH_3)_2$), 69.8 (=C-CN), 122.5 (=CH), 124.0 (CN), 135.8 (=CH), 153.9 ($C-N(CH_3)_2$).
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10. A very similar chemical shift was reported for C-2 in the imidazolium (CD_2Cl_2) 167.4 ppm in ref. 10.
11. The picrate is a yellow solid which decomposes at 85°C, in acetonitrile solution, however, decomposition occurs already at r.t. Selected ^{13}C NMR data (CD_3CN): $\delta = 166.5$ ($C(N(CH_3)_2)$, 128.8 (=CH), 140.3 (=CH), 39.6 (CH_2), 38.2 ($C(CN)_2$), 31.8 ($C(CN)_2$).

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