Nucleophilic additions of the cyanide anion to 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene

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The unexpected formation of a 2*H*-pyrrole by reaction of potassium cyanide with 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene and the mechanism of this reaction are described and the structures of the product and a trapped intermediate confirmed by X-ray crystallographic studies.

Keywords: potassium cyanide, 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene

As a part of our research on the reactivity of the 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene **1** towards nucleophiles, we have previously described reactions with some sodium alkoxides.[2] To our knowledge, the only other examples of nucleophilic attack on substituted 2-azabutadienes **1** have been reported by Lorente *et al*.[8]

The azadiene **2** is heated in a saturated solution of potassium cyanide in DMF for 3 hours. After washing with water and ether extraction, the crude solid residue is recrystallised from ethanol. The spectroscopic data were not sufficient to establish the structure of this compound. An X-ray analysis allowed us to identify its structure as 3-amino-4,5-dicyano-2,2-diphenyl-2*H*-pyrrole **12** (Fig.1).[9]

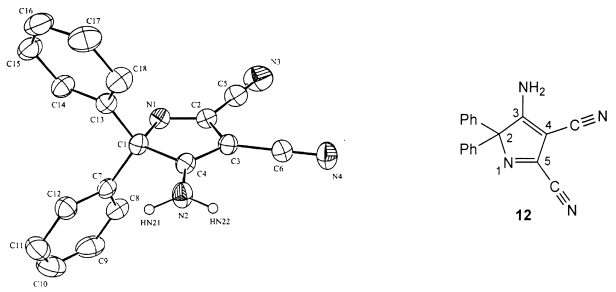


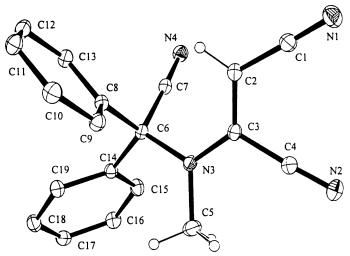
Fig. 1 Ortep diagram of the structure of the 2*H*-pyrrole **12**. $C_{18}H_{12}N_4$, monoclinic, $P2_1/c$, final R indices $R_1 = 0.044$; $wR_2 = 0.109$. Selected bond lengths (Å) and angles (°): C1–N1 1.483(2), N1–C2 1.284(2), C2–C3 1.455(2), C3–C4 1.371(2), C4–C1 1.528(2), C2–C5 1.440(2), C5–N3 1.137(2), C3–C6 1.413(2), C6–N4 1.139(2), C4–N2 1.325(2), N1–C2–C3 116.19(14), C2–C3–C4 105.25(13), C3–C4–C1 107.41(12), C4–C1–N1 105.02(12), C2–C5–N3 179.0(2), C3–C6–N4 179.12(18).

The comparison between the formula of this 2*H*-pyrrole **12** and that of the azadiene **2** indicates that three cyanide anions have reacted. Moreover, the ORTEP diagram proves that the three attacks occur at the three electrophilic centres C(1), C(3) and C(4) of the azadiene **2**. The first attack can take place at one of these three centres and the second addition at one of the two remaining positions. Examination of the six possibilities allows us to propose the unique mechanism leading to the established structure (Scheme 4).

As in the case of alkoxides, the reaction with cyanide begins by a nucleophilic attack of the cyanide at the C(3) carbon atom of the azadienic linkage, providing the intermediate **[13]**, which is in equilibrium with its tautomeric form **[14]**. The second nucleophilic attack of the cyanide takes place at the C(4) carbon atom of the azadienic intermediate **[15]** to give **[16]**. Here, a third attack on the neutral species **[16]** becomes possible and occurs at the C(1) carbon atom. The anionic species **[17]** contains both nucleophilic and electrophilic centres, and so, cyclisation may occur.

A similar cyclisation was previously observed by Lorente and coworkers.[8d]

In order to confirm the mechanism of formation of the 2*H*-pyrrole **12**, we have tried to trap an anionic intermediate before the ring closure as **[17]** or after the cyclisation as **[18]** or **[18′]**. The reaction was carried out as described above, but before the final hydrolysis, a large excess of methyl iodide was added. After the usual workup, a solid compound was isolated for which the structure **24** was established by an X-ray crystallographic study (Fig.2).[9]



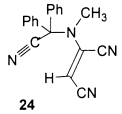


Fig. 2 Ortep diagram of the structure of the product **24**. $C_{19}H_{14}N_4$, triclinic, P-1, final R indices $R_1 = 0.0387$; $wR_2 = 0.0984$. Selected bond lengths (Å) and angles (°): C6–N3 1.4843(13), N3–C3 1.3636(14), C3–C2 1.360(2), C2–C1 1.420(2), C1–N1 1.150(2), C3–C4 1.4534(15), C4–N2 1.1444(15), C6–C7 1.5039(15), C7–N4 1.1449(15), N3–C5 1.4664(15), C2–C1–N1 177.73(13), C3–C2–C1 120.59(10), C2–C3–C4 116.87(10), C3–C4–N2 176.67(12), C3–N3–C5 119.41(9), C5–N3–C6 120.94(9), N3–C6–C7 107.59(8), C6–C7–N4 177.97(11).

This result is consistent with the existence of the transient anion **[17]** (Scheme 6) and the methylation occurs at the imino-nitrogen atom before the ring-closure process. The closure takes place on treatment with water.

The first attack of cyanide occurs then at the C(3) carbon atom, in the same manner as we have previously observed with alkoxides.[2] But, contrary to reaction with alkoxides, the second attack takes place at the position (4), in good agreement with the more stable resonance structure in the intermediate **[15]** (Scheme 7).

Thus, the two strong electron-withdrawing nitrile groups make the C(1) sufficiently electrophilic to allow the last attack on the transient species **[15]**.

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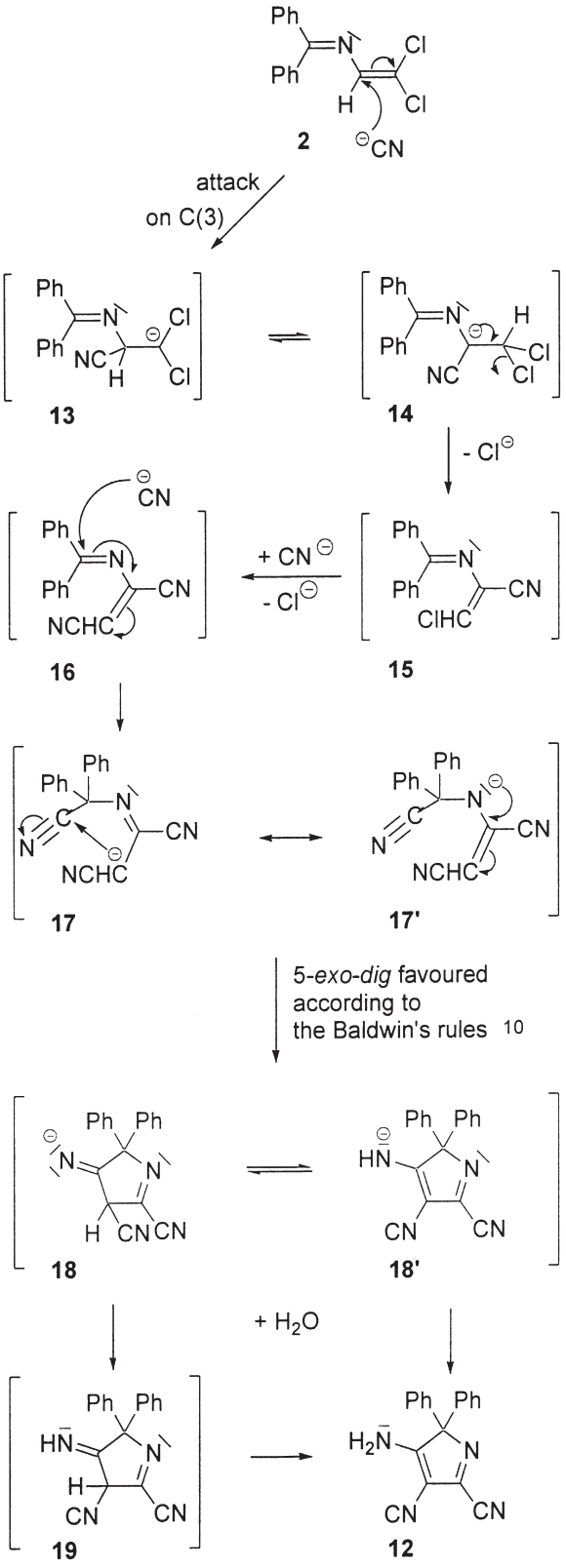
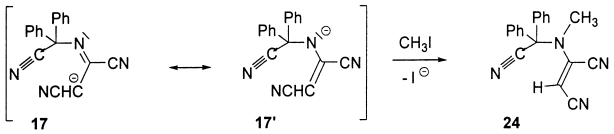
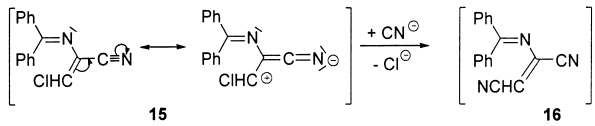


Scheme 4 Mechanism of the addition reaction of the cyanide anion to the azadiene **2**.



Scheme 6 Methylation of the transient anion [**17** ↔ **17′**].



Scheme 7 Resonance in the intermediate **[15]**.

This work has established the mechanism of nucleophilic reactions of potassium cyanide on 4,4-dichloro-1,1-diphenyl-2-azabuta-1,3-diene. We have shown that it consists of a first nucleophilic addition at the C(3) carbon atom of the azadiene **2**, followed by a second at the position (4) and finally a intramolecular nucleophilic attack at the C(1) carbon atom, which affords the carbanion **[17]** allowing the cyclisation by an intramolecular nucleophilic attack.

Techniques used : IR, ^{1}H and ^{13}C NMR data, X-ray diffraction

References : 10

Schemes : 7

Figures : 2

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9 Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-164902 **(12)** and CCDC-164903 **(24)**. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: (internat. + 44-1223/336-033; E-mail : deposit@ccdc.ac.uk]

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