

Nitrene-like Behaviour of Diazoazoles?

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Treatment of 4,5-dicyano-2-diazoimidazole, 2-diazoimidazole, and 3-diazopyrazole with 1,1-dimethoxyethene affords azolo-*as*-triazines (**1c**), (**3c**), and (**8c**), respectively; the involvement as intermediates of either aziridines (**d**), arising from a 'nitrene-like reaction' of diazoazoles, or azoalkenes (**b**) should be questioned at present.

Nitrene-like behaviour has been postulated recently for 4,5-dicyano-2-diazoimidazole (DDI) in its reaction with 1,1-dimethoxyethene and 2,3-dimethylbuta-1,3-diene.¹ Such a suggestion is rather striking, bearing in mind the well-established 1,3-dipolar character² of diazo compounds and the participation of diazo groups in typical azo-coupling and

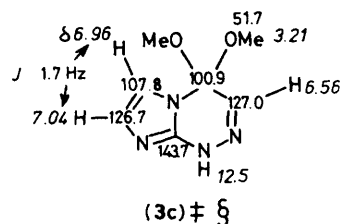
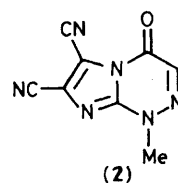
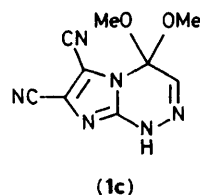
related electrocyclic reactions.³ In fact, these two pathways can also be envisaged for the first step, see (**a**) and (**b**), of the reaction of diazoazoles (*e.g.*, 2-diazoimidazole,⁴ 2-DI) with polar alkenes (*e.g.*, 1,1-dimethoxyethene). Moreover, several examples are known of the formation of 1,7-cycloadducts or azolo-*as*-triazine derivatives⁵ from diazoazoles and activated

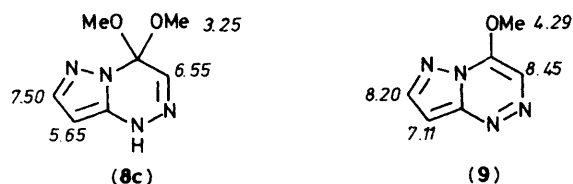
double or triple bonds, according to (c). 'Formal nitrene-like behaviour,' which could be represented by (d), has been demonstrated for some diazoalkenes,^{6,7} but it is quite untenable that a diazo group reacts as a standard nitrene. As a matter of fact, all the intermediates shown in (a)–(d) may be interconverted through one- or two-step reactions. However, what kind of evidence supports pathway (d) for DDI and/or other diazoazoles?

We have found that when DDI was treated with 1,1-dimethoxyethene [isolated in 51% yield after distillation from the reaction of bromoacetaldehyde dimethyl acetal and NaH in hexamethylphosphoric triamide (HMPT) at 80–90°C] in benzene at room temperature¹ a colourless product was obtained in very good yield [m.p. 192°C (decomp.); δ 7.15 (1H, s) and 3.40 (6H, s) in (CD₃)₂CO; δ 6.93 (1H, s) and 3.30 (6H, s) in MeCN], which showed its two equivalent methyl carbons at δ 52.3, a methine carbon at δ 130.0, and six quaternary carbon atoms at δ 144.5, 122.5, 112.1, 108.3, 102.0, and 101.5. Structure (1c) rather than (1b)¹ must be attributed to the product since among other arguments: (i) the non-equivalence of carbons C-4 and C-5 of the imidazole ring and of the two cyano substituents is only compatible with an N-substituted azole ring; (ii) the expected δ value for the olefinic C(OMe)₂ carbon atom of (1b) is *ca.* 180 p.p.m.,⁸ whereas the carbon at lower field is found at δ 144.5 (and, furthermore, it corresponds to C-2 of the imidazole ring); (iii) the olefinic proton of (1b) should appear at δ 5.4, taking into

account the shift of 2.4 p.p.m. induced by a phenylazo substituent on geminal olefinic protons⁹ (note that the olefinic protons of 1,1-dimethoxyethene appear at δ 3.00 in CDCl₃), perhaps even in the δ 5.5–6.0 range, but never at δ 6.5–7.0. Heating of (1c) either in refluxing xylene, in a sealed tube with benzene at 150°C,¹ or without solvent to 170°C gave, as the major product, 6,7-dicyano-1-methylimidazo[2,1-c]-as-triazin-4-one, (2), m.p. 218–219°C, ν (C=O) 1710 cm⁻¹, δ 7.84 (1H, s) and 4.15 (3H, s) in (CD₃)₂CO.

In a similar way, when 2-DI was treated, in benzene at room temperature, with 3 equiv. of 1,1-dimethoxyethene, the solution turned reddish† but a colourless product, m.p. 137–140°C, m/z 182 (*M*⁺), was obtained in 70–81% yields





after two recrystallisations of the reaction residue from CH_2Cl_2 –pentane; its 200 MHz ^1H n.m.r. and 50.3 MHz ^{13}C n.m.r. spectra in CDCl_3 (having two equivalent methoxy groups, three methines, and two quarternary carbons) showed clearly that the product was (3c) and ruled out (3a), (3b), and (3d).

To confirm structure (3c), 2-DI labelled with 25% of ^{15}N at N_β (starting from 2-aminoimidazole sulphate⁴ and commercial $\text{Na}^{15}\text{NO}_2$) was allowed to react with an excess of 1,1-dimethoxyethene as above, affording a major compound to which structure (3c/3c*) was assigned in view of its ^1H , ^{13}C , and ^{15}N n.m.r. spectra: (i) the proton signal at δ 6.56 shows a lateral doublet due to the ^1H – ^{15}N splitting with $|J|$ 14.2 Hz; (ii) the carbon signal at δ 127.0 is also split ($|J|$ 2.3 Hz); (iii) the proton-undecoupled ^{15}N signal appears as a doublet, $|J|$ 14.2 Hz, at δ –42.4 (i.e. 42.4 p.p.m. to higher field than 10 M H^{15}NO_3 , the external reference). These J values agree perfectly with those found for pyridine and other azine and imine derivatives.¹⁰ Moreover, the ^{15}N chemical shift of the labelled nitrogen lies in the expected zone for (3c*), whereas that expected for (3b*) is 145–215 p.p.m., at lower field than H^{15}NO_3 .¹⁰

The reaction of 2-DI with 1,1-dimethoxyethene was also monitored by ^1H n.m.r. spectroscopy in C_6D_6 at 0–5 °C. The proton signals of the reagents disappeared in several minutes, but only the signals corresponding to (3c), which increased throughout the experiment, could be detected in the aromatic and olefinic regions of the spectrum. Intermediates (3a), (3b), and/or (3d) might be involved, but their half-lives seem to be too short under these conditions to allow their detection.

Attempts to purify (3c) by column chromatography on silica gel, instead of by recrystallisation, with CH_2Cl_2 –MeOH (99:1) as the eluant, caused its partial transformation into a product showing three aromatic protons and only one methoxy group, to which structure (4) must be assigned, as well as into minor amounts of 1-methylimidazo[2,1-c]-as-triazin-4-one, (5) and its isomers (6) and (7), as deduced by comparison (t.l.c. and ^1H n.m.r.) with authentic samples of (5)–(7) obtained by other routes.¹¹ Moreover, a mixture of (5)–(7) was produced by heating (3c) in refluxing benzene for several hours. Compound (4) was also converted into the above-mentioned mixture by heating.¹² Thus, the sequence (3c) \rightarrow (4) \rightarrow (5) + (6) + (7) appears to be sound.

Similarly, when 3-diazopyrazole (3-DP) and an excess of 1,1-dimethoxyethene were allowed to react in CH_2Cl_2 or benzene at room temperature for 45 min, (8c) was obtained.

Upon standing, even in the n.m.r. tube in CDCl_3 , (8c) lost MeOH and was (partially) converted into (9).

In conclusion, there is no evidence for the formation of species (b) or (d). The involvement of aziridines (d) as intermediates,^{||} which would suggest a nitrene-like behaviour of diazoazoles, has also to be proved yet.

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^{||} According to MNDO SCF-MO calculations (refs. 13 and 14), species (d) are predicted to lie ca. 160 kJ mol^{–1} above (c). Thus, such aziridine intermediates are unlikely.