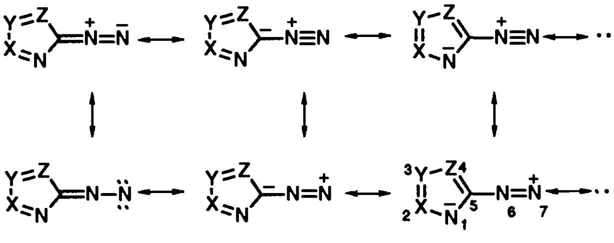
Reactivity of Diazoazoles with Electron-rich Double Bonds

Marta Cabré,[a] **Jaume Farràs,***[a] **Javier Fernández Sanz**[b] **and Jaume Vilarrasa**[a]
[a] *Departament de Química Orgànica, Facultat de Química, Universitat de Barcelona (III), 08028 Barcelona, Catalonia, Spain*
[b] *Departamento de Química Física, Facultad de Química, Universidad de Sevilla, 41071 Sevilla, Andalucía, Spain*

The energies of several intermediates that could arise from the reaction of diazoazoles with alkenes have been estimated by means of the MNDO and AM1 SCF-MO methods as well as, in some cases, by means of *ab initio* methods, at the 3-21G level. All the nine possible unsubstituted diazoazoles have also been calculated by MNDO and their similarities and differences, among them and with regard to diazomethane and 4,5-dicyano-2-diazo-2*H*-imidazole, have been discussed. The calculations suggest a 1,4-dipole behaviour (also viewed as a 1,7-dipole behaviour) for most diazoazoles when reacting with electron-rich alkenes; it is believed that the approach between 2-diazo-2*H*-imidazole and alkenes to give rise to the [4 + 2]-cycloadducts is quite asynchronous. Finally, some errors found in the literature concerning the reactivity of diazoazoles with alkoxyethenes have been corrected, while the reactivity of certain diazoazoles with conjugated dienes to afford *N*-azolodihydropyridazines rather than azolotriazine derivatives (*via* 'reverse electron demand' cycloadditions) has been confirmed.

It is generally accepted that diazoazoles with the diazo group at position α to a ring nitrogen (**1**), if nitrogen extrusion is avoided, may react as 1,2-dipoles, 1,3-dipoles, or 1,4-dipoles (1,7-dipoles) with suitable unsaturated compounds.[1] In theory, an electron-rich alkene of general formula $CH_2{=}CRR'$ [(**2**), R and/or R′ = electron-donating groups] may react regioselectively with substrates (**1**) to afford the following intermediates and/or products: the aziridines (**3**), arising from [1 + 2]-cycloadditions; the four-membered betaines (**4**), which could be in equilibrium with their tautomers (**4′**); the [3 + 2]-cycloadducts (**5**), from which tautomers (**5′**) may be derived; species (**6**), containing a six-membered ring, and their tautomers (**6′**); and azo-coupling products labelled as (**7′**) and (**7″**), arising from betaine-like intermediates (**7**). On the other hand, an electron-deficient alkene [(**2**), R and/or R′ = electron-withdrawing groups] might react with substrates (**1**) to afford as main intermediates the alternative regioisomers of (**5**) and (**6**) (not shown in the formulae).



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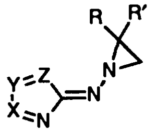
Since formation of five- and six-membered rings may be relatively favoured as a general rule, we shall comment first on these possibilities. As a matter of fact, the plausible involvement of species (**5**) in the chemistry of diazoazoles was suggested in former reports,[2–5] but these species were never isolated. By contrast, isolation of azolotriazine systems related to (**6**) and (**6′**) has been widely demonstrated.[3–10] Thus, it seems that, in opposition to the reactivity of diazocyclopentadiene, which shows a tendency to be involved in [3 + 2]-cycloadditions,[11] diazoazoles of type (**1**) tend to afford either directly or eventually [4 + 2]-cycloadducts (also called 1,7-cycloadducts[8]).



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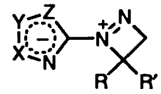

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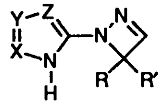
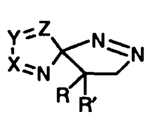


4′



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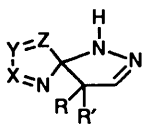
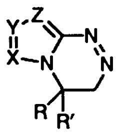


5′



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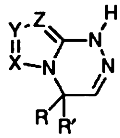
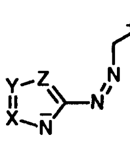


6′



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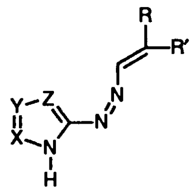
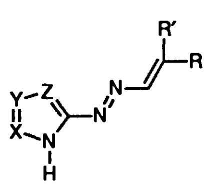


7′



7″

a;	X = Y = CH,	Z = N,	R = R′ = H
b;	X = Y = CH,	Z = N,	R = OH, R′ = H
c;	X = Y = CH,	Z = N,	R = R′ = OH
d;	Y = X = CH,	X = N,	R = R′ = OH
e;	X = Z = N,	Y = CH,	R = R′ = OH
f;	X = Y = C(CN),	Z = N,	R = R′ = OH

Concerning the remaining possible intermediates, it should be noted that aziridine intermediates (**3**) might be formed[12] in the same way that certain diazo alkenes undergo an intramolecular cyclisation,[13] either stepwise or concerted, to 1,2-diazabicyclo[3.1.0]hex-2-enes; structures (**3**) suggest a nitrene-like behaviour of diazoazoles,[12] as if the 'nitrene' canonical form of compounds (**1**) was a major factor in the diazoazole reactivity. The chance of formation of four-membered species (**4**), either from a kinetic or thermodynamic point of view, is thought to be very low; in fact, there are no known examples of

Table 1. Energies of intermediates and products arising from reaction of 2-diazo-2*H*-imidazole (2DI) with ethene.[a]

	MNDO	Corr.[b]	E_r	AM1	Corr.[b]	E_r	3-21G‖MNDO	E_r	3-21G‖STO-3G	E_r
(3a)	109.0	109	40	155.5	156	49	−408.131 19	67.4	−408.140 40	68.2
(4a)	119.7	120	51	177.9	178	71	−408.129 43	68.5		
(4a′)	97.2	97	28	153.0	153	46	−408.173 44	40.9		
(5a)	72.9	83	14	119.7	129	22	−408.190 60	30.1	−408.194 89	34.0
(5a′)	81.7	82	13	126.2	126	19	−408.200 54	23.9	−408.211 15	23.8
(6a)	67.8	78	9	105.6	115	8	−408.206 70	20.0	−408.212 28	23.1
(6a′)	68.9	69	0	107.0	107	0	−408.238 63	0	−408.249 14	0
(7a′)	85.8	96	27	114.6	>124[c]	>17[c]	−408.192 02	29.2		
(7a″)	84.0	91[d]	22	123.9	124	17	−408.207 00	19.8	−408.208 17	25.7

[a] Heats of formation (MNDO and AM1) and relative energies (E_r) in kcal mol^{-1} (1 kcal = 4.184 kJ); 3-21G total energies in au (1 au = 2625.5 kJ mol^{-1}). [b] Corrected MNDO and AM1 values (refs. 16 and 17). [c] It is thought that the correction term should, in this case, be 9 kcal mol^{-1} at least (as for vicinal pyridine-like nitrogens) and probably higher, taking into account that (*E*)-azo compounds are usually more stable than their (*Z*)-isomers (for azobenzenes, see ref. 20). [d] No systematic evaluation of the MNDO errors concerning (*E*) azo derivatives has ever been reported, but a correction term of *ca.* 7 kcal mol^{-1} could be assumed after comparison of the MNDO-calculated and experimental heats of formation of azopropane and azoisopropane (ref. 15).

Table 2. Energies of intermediates and products arising from 2DI and hydroxyethene.[a]

	MNDO	Corr.	E_r	AM1	Corr.	E_r	3-21G‖MNDO	E_r
(3b)	59.7	60	38	108.9	109	47	−482.569 17	68.6
(5b)	31.7	42	20	77.5	87	25	−482.613 95	40.5
(5b′)	38.5	38	16	81.8	82	20	−482.632 37	28.9
(6b)	22.0	32	10	60.5	70	8	−482.647 04	19.7
(6b′)	22.3	22	0	62.5	62	0	−482.678 44	0
(7b′)	34.5[b]	44	22	66.8[b]	>76[c]	>14[c]	−482.630 02	30.4
(7b″)	32.3[b]	39[d]	17	75.9[b]	76	14	−482.643 54	21.9

[a] See footnote *a* in Table 1. [b] The all-*trans* C=C–O–H planar arrangement; other configurations and conformations at ±2 kcal mol^{-1}. [c] See footnote *c* in Table 1. [d] See footnote *d* in Table 1.

compounds (**4**) and (**4′**). Finally, we should add that azo-coupling products have also been proposed,[12,14] probably on the basis that diazo compounds with strongly electron-withdrawing substituents may behave as standard diazonium salts against electron-rich alkenes to yield compounds (**7′**), which may isomerise *in situ* to the more stable (*E*) isomers (**7″**).

In the present work we have considered all these reaction pathways. First, theoretical calculations at the semiempirical and *ab initio* levels were performed on the most plausible reaction intermediates and/or their main tautomers, with the purpose of predicting which of them will have lower total energies; the species with the highest calculated total energy have not been so systematically evaluated. After a discussion of the transition states involved, a few experiments have been performed to corroborate these theoretical predictions and to evaluate earlier literature data.

Computational Procedures.—The MOPAC and AMPAC packages have been used for MNDO and AM1 calculations.[15] All equilibrium geometries were determined by minimising the total energy with respect to all geometrical variables, including dihedral angles, unless otherwise indicated. All the structures reported here are true relative energy minima, according to the corresponding vibrational analysis. As evaluated previously,[16] the MNDO-calculated heats of formation for azoles agree fairly well with the experimental values provided that, for those five-membered rings with neighbouring pyridine-like nitrogens, a correction term of *ca.* 10 kcal mol^{-1} * is added to the calculated value, for each such pair of vicinal nitrogens. The AM1 method, as far as heterocycles are concerned, has also been evaluated previously by some of us.[17] Six-membered rings are appropriately described by AM1 (more reliably than by MNDO), provided again that a correction term of *ca.* 9 kcal mol^{-1} for each pair of vicinal nitrogens is added to the calculated ΔH_f-values; however, the ΔH_f-values calculated for five-membered rings are much higher than the available experimental ones. In spite of this important shortcoming of AM1, we have also used this method because our experience indicated that even though the calculated absolute energies of five-membered heterocycles were nonsense, the relative energies were reasonable.

Geometry optimisations with a minimal basis set (STO-3G)[18] have also been performed for some intermediates. Calculations with the 3-21G split-valence basis set[19] at the MNDO and STO-3G geometries (henceforward called 3-21G‖MNDO and 3-21G‖STO-3G calculations) have been performed in selected cases to check the MNDO and AM1 results. The reliability of these approaches in the field of heterocycles has been previously evaluated.[17]

Results and Discussion

First of all, possible intermediates arising from the imaginary reaction of 2-diazo-2*H*-imidazole (2DI) and ethene, as well as some significant tautomers of these reaction intermediates, were calculated by the MNDO and AM1 methods. The corresponding ΔH_f-values are collected in Table 1, and their relative energies are compared with those derived from the 3-21G‖MNDO and 3-21G‖STO-3G calculations. Table 2 shows the energies calculated by MNDO, AM1, and 3-21G‖MNDO for intermediates and products arising from the reaction of 2DI and hydroxyethene, a model for ethyl vinyl ether. Finally, the energies calculated at the MNDO level for species coming from the reaction of 1,1-dihydroxyethene with 2DI, with 3-diazo-3*H*-pyrazole, with 3-diazo-3*H*-1,2,4-triazole, and with 4,5-dicyano-2-diazo-2*H*-imidazole (DDI) are collected in Table 3; we used 1,1-dihydroxyethene as a model for a polar dialkoxyalkene such as 1,1-dimethoxyethene. It should be noted that in the case of the

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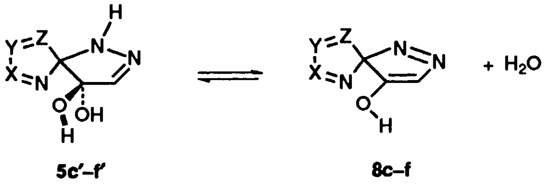
* 1 cal = 4.184 J.

Table 3. Energies of intermediates and products arising from 1,1-dihydroxyethene and 2DI (series **c**), 3-diazo-3*H*-pyrazole (**d**), 3-diazo-3*H*-1,2,4-triazole (**e**), and 4,5-dicyano-2-diazo-2*H*-imidazole (DDI) (**f**), respectively.[a]

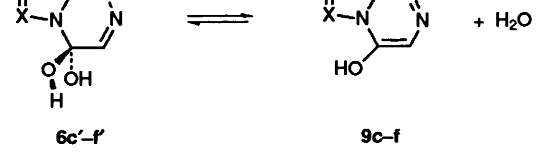
	MNDO	Corr.	E_r		MNDO	Corr.	E_r
(3c)	9.4	9	35	**(3d)**	15.6	26	43
(4c)	16.8	17	42	**(4d)**	22.6	33	50
(4c′)	−0.7	−1	25	**(4d′)**	13.1	13	30
(5c)	−13.8	−4	22	**(5d)**	−5.5	14	31
(5c′)	−6.2	−6	20	**(5d′)**	4.1	14	31
(6c)	−26.4	−16	10	**(6d)**	−19.4	−9	8
(6c′)	−26.3	−26	0	**(6d′)**	−17.1	−17	0
(7c′)	-17.9^b	−8	18	**(7d′)**	-2.9^b	7	24
(7c″)	-18.8^b	-12^c	14	**(7d″)**	-8.0^b	-1^c	16
(8c)	58.2	68	94 (33)[d]	**(8d)**	65.7	86	103 (42)[d]
(9c)	35.4	45	71 (10)[d]	**(9d)**	42.4	52	69 (8)[d]
(3e)	18.8	29	47	**(3f)**	74.8	75	39
(4e)	23.7	34	52	**(4f)**	76.5	77	41
(4e′)	10.7	11	29	**(4f′)**	57.5	58	22
(5e)	−5.1	15	33	**(5f)**	53.8	64	28
(5e′)	1.6	12	30	**(5f′)**	61.4	61	25
(6e)	−16.6	−7	11	**(6f)**	37.3	47	11
(6e′)	−17.8	−18	0	**(6f′)**	36.0	36	0
(7e′)	$-6.8^{b,e}$	3	21	**(7f′)**	41.8^b	52	16
(7e″)	$-7.9^{b,e}$	-1^c	17	**(7f″)**	40.5^b	47^c	11
(8e)	67.4	87	105 (44)[d]	**(8f)**	126.7	136	101 (40)[d]
(9e)	47.1	57	75 (14)[d]	**(9f)**	99.8	110	74 (13)[d]

[a] Similar E_r (all energies in kcal mol^{-1}) are obtained at the AM1 level. [b] Planar conformations, avoiding hydrogen bonds as far as possible. [c] See footnote *c* in Table 1. [d] Values within parentheses include ΔH_f-value of water (see the main text). [e] Tautomer 1*H*.

hydroxy derivatives, in which different conformations by rotation around C–O bonds are possible, the trial geometries were chosen to avoid N···H–O and O···H–O hydrogen bonds (which are absent, of course, in the products arising from ethyl vinyl ether and 1,1-dimethoxylethene); subsequent optimisations gave comparable relative energy minima lacking these undesired hydrogen bonds. Also in Table 3, we have included the ΔH_f-values for the dehydration products 4-hydroxy-1,2,6,9-tetra-azaspiro[4.4]nonatetraene and related derivatives (**8c–f**) and 4-hydroxyimidazo[2,1-*c*][1,2,4]triazine and related derivatives (**9c–f**), with the purpose of evaluating the approximate heats of reaction associated with the following reactions, which could serve as models for alkoxy and similar derivatives.



5c′–f′ **8c–f**



6c′–f′ **9c–f**

In comparing the semiempirical and *ab initio* relative energies shown in Tables 1 and 2, it appears that they correlate fairly well, even though MNDO and AM1 predict lower energy gaps among the different intermediates. Qualitatively, the agreement among Tables 1, 2, and 3 is good:

(i) The azolotriazine derivatives (**6a′**)–(**6f′**) lie quite below those of the respective remaining species.

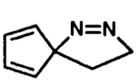
(ii) By comparison of tautomers (**6a**) with (**6a′**), (**6b**) with (**6b′**), and so on, it appears that the latter ones are 8–11 kcal mol^{-1} lower in energy, according to the semiempirical methods, or 20–30 kcal mol^{-1} lower, according to the *ab initio* results (*i.e.*, the hydrazone arrangement is predicted to be more stable than the azo derivative substructure, as is generally accepted).

(iii) In comparing structures (**3a**), (**4a**), (**5a**) and (**6a**), as well as structures (**3b**), (**4b**), (**5b**) and (**6b**), and so on, it turns out that the azolotriazine intermediates—those that may arise from a [4 + 2]-cycloaddition—are always predicted to be the preferred ones. By contrast, in agreement with qualitative predictions in view of the ring size, the intermediates arising from [1 + 2]-cycloadditions and from formal [2+2]-cycloadditions have far higher energies. The chance of detecting these initial intermediates (**3**) and (**4**) must be very low, not only because they would isomerise rapidly and irreversibly to products (**6**) or other intermediates of lower energy, but also because their preceding transition states must have a higher total energy.

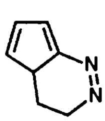
(iv) The case of the [3 + 2]-cycloadducts (**5**) deserves special comment, since they are closer to compounds (**6**) in energy. At the MNDO level the gap is only 5 kcal mol^{-1} for series **a** (but 10 kcal mol^{-1} at the 3-21G level), 10 kcal mol^{-1} for series **b** (but 20 kcal mol^{-1} at the 3-21G level), 12 kcal mol^{-1} for series **c**, 23 kcal mol^{-1} for series **d**, and so on. It seems that the more polar or substituted is the alkene, the more unstable are the spiranes (**5**), as if electronic repulsions in the more sterically crowded or congested spiranes increased the energy difference. Bearing in mind only the thermodynamic data discussed so far, it cannot be ruled out that in certain cases [3 + 2]-cycloadducts (**5**) were formed first and then underwent isomerisation to the thermodynamically more stable [4 + 2]-cycloadducts (**6**).

At this point it is interesting to comment on the diazocyclopentadiene case, whose tendency to be involved in [3 + 2]-cycloadditions is known.[11] We have calculated at the MNDO level the [3 + 2]-cycloadduct (**5g**) and [4+2]-cycloadduct

(**6g**). The ΔH_f-values are 65.4 and 62.6 kcal mol^{-1}, respectively. Analogously, for (**5h**) and (**6h**), the ΔH_f-values are -20.6 and -23.6 kcal mol^{-1}, respectively. Thus, the gaps are smaller than those found in the diazoazoles considered above ('α-diazoazoles'). It is reasonable to believe that in the case of these diazoazoles the presence of nitrogen atoms (electronegative but nucleophilic) in the ring, as well as the maintenance of the aromaticity of the azole ring, favour even more, from both the kinetic and thermodynamic points of view, the azolotriazine structures with regard to the spirane intermediates. When 5-diazo-1,4-dimethylcyclopenta-1,3-diene instead of the parent diazocyclopentadiene was employed in the calculations, the relative energies of the [3 + 2]-cycloadduct and [4 + 2]-cycloadduct are reversed (the respective ΔH_f-values are now 48.6 and 53.6 kcal mol^{-1}); owing to the poor description of crowded molecules by MNDO,[15] these values are not very reliable but the trend is clear and reasonable: substituents at positions α with regard to the diazo group may disfavour those cycloadditions that involve these positions.



5g



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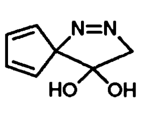
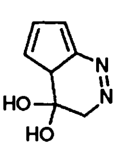


5h



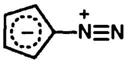
6h

The (Z) azo compounds (**7′**) are systematically predicted to lie far above compounds (**6**), but at least for the more polar substrates derived from 1,1-dihydroxyethene (series **c**–**f**) the corresponding (Z) azo compounds are calculated to be more stable than the remaining initial cycloadducts. The (E) azo compounds (**7″**), to which their (Z) analogues could be isomerised, are even more stable, as expected.[20] In other words, it seems that from a thermodynamic point of view the formation of open intermediates should be the second possibility to be considered after that of [4 + 2]-cycloadducts. However, a note of caution should be added: the initial intermediates arising from a net azo coupling reaction are the betaines (**7**) rather than azo compounds (**7′**), and the energies of these betaines are of course really high [*e.g.*, the ΔH_f-value calculated at the MNDO level for (**7a**) is 168.9 kcal mol^{-1}, *i.e.*, 50 kcal mol^{-1} above the most unstable of all the intermediates shown in Table 1]. Thus we believe that azo coupling occurs only in polar and protic media, where those betaine forms can be stabilised by solvation and/or by concomitant protonation of the azole ring as far as both reagents interact (the diazoazole thus behaving as a diazonium salt).

(vi) Finally, concerning the dehydration products (**8c**–**f**) and (**9c**–**f**), it turns out that the processes are endothermic [by ~8 and 14 kcal mol^{-1} at the MNDO level for the (**6′**) $\rightleftharpoons$ (**9**) + H_2O case, in spite of the apparently higher aromaticity of compounds (**9**)]. In practice it has been observed that the loss of one alcohol molecule from the dialkoxy derivatives related to compounds (**9**) is an equilibrium generally not shifted to the right at room temperature.[9,10,21] Nevertheless, analogous pyrazole derivatives undergo elimination of alcohol more readily,[5,9] which may be explained on the basis of the differences shown in Table 3, where it is seen that compound (**9d**) is relatively more stable than compounds (**9c**), (**9e**), and (**9f**), probably owing to the lack of a nitrogen at position 8.

Predictions regarding the Main Mechanisms involved.—Experimentally, there is no doubt that 'α-diazoazoles' react with electron-rich alkenes to give compounds of type (**6′**) as the main or unique isolated products.[3–10] Theoretically, as just disclosed here, compounds (**6**) are thermodynamically favoured among the possible initial intermediates. However, there remains the possibility that under kinetic control conditions compounds (**5**), or even (**7**) in very polar solvents, were formed first, and then underwent quick isomerisation or cyclisation to give products (**6**).

An approach to this question may be based on the frontier orbital theory. For this purpose we have calculated at the MNDO level the energy of diazocyclopentadiene (**10**),[22] its nine possible aza derivatives, (**11**)–(**19**) and for comparison, 4,5-dicyano-2-diazo-2*H*-imidazole (DDI) (**20**), a compound used in earlier experimental studies,[12,14] and diazomethane (**21**). Their heats of formation, HOMO and LUMO energies, main bond distances, π-electron densities and atomic net charges, and dipole moments are shown in Table 4, while the HOMO and LUMO coefficients, closely related for all the members of the series, are shown in Fig. 1.



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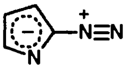

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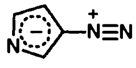

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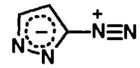

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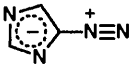

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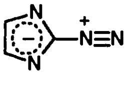

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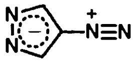

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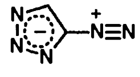

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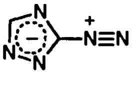

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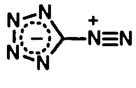

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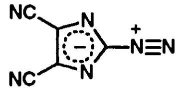


20

CH_2N_2

21

Although the LUMO–HOMO gaps are maintained along the series (8.3 ± 0.3 eV), the energies of these MOs become more negative when the ring contains more and more nitrogen atoms, as expected; the gap is a bit lower for DDI (**20**) and quite higher for diazomethane, which is also reasonable for a more and less conjugated diazo derivative, respectively. These HOMOs and LUMOs are π orbitals (π_z*), a second lowest unoccupied MO ('LUMO$_2$') that involved the in-plane p-AOs of N_β and N_α (π_y*) being found only 0.4 ± 0.1 eV above; as an exception, in the case of diazomethane this π_y* orbital appears to be the first LUMO. All the LUMO coefficients of compounds (**10**)–(**20**) can be summarised as in Figs. 1(*a*) and 1(*b*). By contrast, some differences are found in the HOMOs from some species to others, since only the diazoazoles possessing the C_{2v}) (or almost C_{2v}) symmetry show the same symmetry in the AO coefficients of the HOMOs, as seen in Fig. 1(*c*).

When the $C^5N^\alpha N^\beta$ bond angle of a few diazoazoles was forced to be 150°, maintaining all atoms in the same plane, and the rest of parameters were optimised in the usual way, the ΔH_f calculated values increased only by 6 ± 1 kcal mol^{-1} and no significant changes were observed in the HOMO and LUMO eigenvectors and eigenvalues. Experimentally, this may imply that, at the common reaction temperatures, owing to the (bending) vibrational energy of the diazo group, the geometry of the true reacting species may resemble more that of *cisoid* butadiene than that of but-1-en-3-yne.

In Fig. 2 we have represented the predominant HOMO–LUMO interactions in the reaction of diazoazoles with alkenes, at the MNDO level. The supra–supra interaction between the LUMO of 2DI (**15**) and of most diazoazoles (if not all) with the HOMO of electron-rich alkenes, which apparently tend to give [4 + 2]-cycloadditions with reverse electron demand, could 'control' the first reaction steps. This and the reasoning posed in the preceding paragraph suggest an approach of the reagents as represented by structure (**22**), leading probably to a quite asynchronous transition state for the reaction of compound (**15**) with electron-rich alkenes.

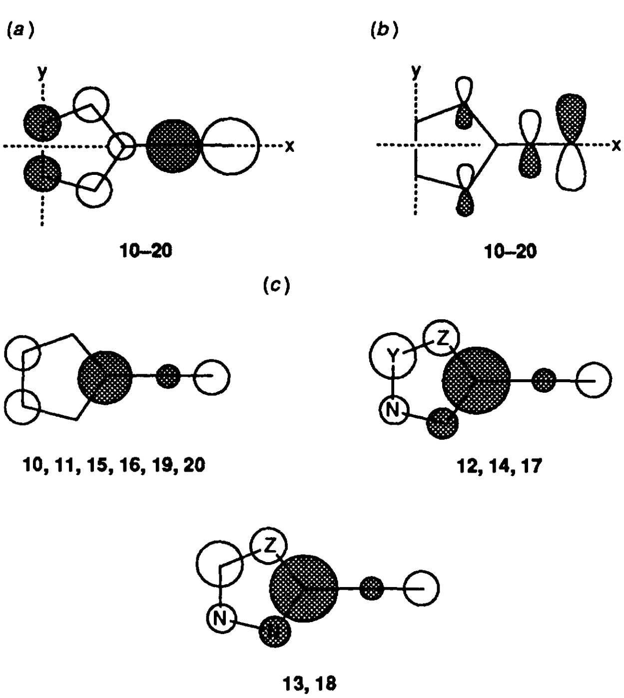


Fig. 1. (*a*) LUMO appearance (π_z*) of compounds (**10**)–(**20**). (*b*) 'LUMO$_2$' (π_y*). (c) The three sets of HOMOs.

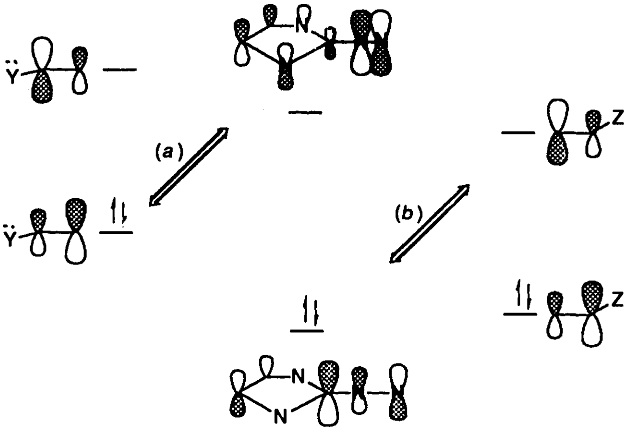
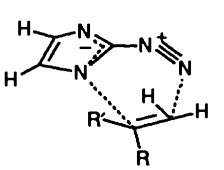


Fig. 2. (*a*) HOMO (electron-rich alkene)–LUMO (**15**) predominant interaction. (*b*) HOMO (**15**)–LUMO (electron-deficient alkene) interaction.



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Alternatively, a perpendicular approach of compound (**15**) and electron-rich alkenes might also be considered in which the HOMO of the alkene would interact with the 'LUMO$_2$' of compound (**15**),[21] but the coefficients of this orbital, as seen in Figure 1(*b*), are not appropriate. From the point of view of frontier orbital theory as well, the supra–supra interaction leading to the [3 + 2]-cycloaddition is less stabilising than that leading to the [4 + 2]-cycloaddition; moreover, the alternative [2 + 2]- and [1 + 2]-cycloadditions are very unlikely.

On the other hand, a good initial interaction between the HOMO of a diazoazole and the LUMO of an alkene could be obtained only if the HOMO was higher in energy and the LUMO of the alkene lower than in the former case. As is known, this would required good donors or no nitrogen atom in the five-membered ring and strong acceptors on the alkene, thus changing the situation from that of reverse to normal electron demand. Only in such a case, according to the HOMOs shown in Figs 1 and 2, may the initial formation of [3 + 2]-cycloadducts be clearly favoured, especially for C_{2v}-like diazoazoles.

The chemistry of diazocyclopentadienes may be accounted for or reinterpreted according to the arguments set out in these last paragraphs. It is believed that 5-diazocyclopenta-1,3-diene and its halogeno, alkyl, or phenyl derivatives may *only* be involved in concerted cycloadditions on reaction with extremely active electron-rich double bonds, to give mainly [4 + 2]-cycloadducts when positions 1 and 4 of the cyclopentadiene are unsubstituted, and to yield mainly [3 + 2]-cycloadducts in the opposite case. On the other hand, 5-diazocyclopenta-1,3-diene and its halogeno, alkyl, or phenyl derivatives should react with sufficiently active electron-deficient double or triple bonds to afford [3 + 2]-cycloadducts as the initial intermediates, which may then lead to [4 + 2]-cycloadducts when positions 1 and 4 do not contain large groups, or to lead to other rearranged products in the opposite case.

It is finally to be noted that the relative triple-bond character of the N$^{\beta}$–N$^{\alpha}$ bond of (**10**)–(**21**) changes moderately but in a logical way: in one extreme, a bond length of 114.1 pm is predicted for diazomethane (**21**), while the more nitrogenated compounds (**19**) and (**20**) are found in the other extreme, both with a bond distance of 111.7 pm. This fact, the almost identical π-electron densities and atomic net charges on the diazo group of compounds (**19**) and (**20**), and their analogously high dipole moments indicate that compound (**20**) may be viewed as a 'less hazardous equivalent' of the powerful explosive diazotetrazole (**19**).

Additional Experimental Results.—As already mentioned, reaction of compounds (**14**), (**15**), (**18**), (**20**), and some derivatives of compounds (**13**), (**17**) and (**18**), with electron-rich double bonds has been shown to afford [4 + 2]-cycloadducts,[3–10] *i.e.* derivatives of structure (**6′**). Other different cycloadducts or open-chain compounds mentioned in some of these reports[5,12] as possible intermediates have been not detected. To corroborate these results as well as the theoretical predictions discussed above, some other experiments have been undertaken.

First of all, the reaction of compound (**20**) with 1,2-dimethoxyethene, which was believed to give an open-chain derivative,[14] has been repeated. The structure of the product actually obtained, in 95% yield, must be attributed to the [4 + 2]-cycloadduct 6,7-dicyano-1,4-dihydro-3,4-dimethoxyimidazo[2,1-*c*][1,2,4]triazine (**23**), in the light of its ^{1}H and ^{13}C NMR spectra (see Experimental section). In other words, as far as the 'rule' of the preference of the highly nitrogenated diazoazoles for [4 + 2]-cycloadditions is concerned, the last exception that remained to be either confirmed or ruled out appears to be an error in assignment.

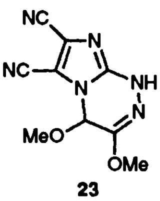
Secondly, the observation that 1,1-dimethoxyethene reacts with diazoazoles such as compounds (**13**), (**15**) and (**20**) to give exclusively [4 + 2]-cycloadducts[9,10] has been corroborated by treatment of 1,1-dimethoxyethene with 3-diazo-3*H*-1,2,4-triazole (**18**) in cold acetone, which afforded a mixture of two isomers: 5,8-dihydro-5,5-dimethoxy[1,2,4]triazolo[3,4-*c*][1,2,4]triazine (**24**), curiously the major product, and 1,4-dihydro-4,4-dimethoxy[1,2,4]triazolo[5,1-*c*][1,2,4]triazine (**25**). On storage in water, compound (**24**) is quantitatively converted into isomer (**25**). [The higher π-electron density and atomic net charge on N-4, in relation to N-1 (see Table 4)

Table 4. Main MNDO results for diazo compounds (**10**)–(**21**).

	ΔH_f[a]	HOMO[b]	LUMO[b]	$N^{\alpha}N^{\beta}$[c]	$N^{\alpha}C^5$[c]	π-Electron density	Net charge[d]	μ_D[e]
(**10**)	97.9	−8.59	−0.60	1.130	1.324	1.339, 1.162 1.317, 1.059	+0.012, +0.161 −0.172, −0.058	0.81
(**11**)	101.6	−8.77	−0.88	1.126	1.333	1.293, 1.152 1.321, 1.195(N^1)	+0.054, +0.182 −0.154, −0.186	2.00
(**12**)	102.7	−8.93	−0.96	1.127	1.328	1.299, 1.149 1.346, 0.945(C^1)	+0.044, +0.180 −0.220, +0.058	3.18
(**13**)	111.9 (*ca.* 122)	−9.43	−1.33	1.123	1.334	1.244, 1.137(C^1) 1.345, 1.097(N^1)	+0.092, +0.205 −0.218, −0.044	4.26
(**14**)	104.2	−9.33	−1.26	1.124	1.332	1.259, 1.142 1.344, 1.224(N^1)	+0.086, +0.200 −0.197, −0.211	3.20
(**15**)	105.1	−9.04	−1.25	1.122	1.337	1.245, 1.143 1.309, 1.173	+0.104, +0.208 −0.124, −0.162	0.59
(**16**)	113.4 (*ca.* 123)	−9.99	−1.39	1.124	1.330	1.257, 1.137 1.374, 0.971	+0.080, +0.198 −0.259, −0.005	5.74
(**17**)	119.5 (*ca.* 140)	−10.31	−1.80	1.120	1.336	1.206, 1.128 1.366, 1.177	+0.130, +0.218 −0.248, −0.080	6.30
(**18**)	112.8 (*ca.* 123)	−9.75	−1.72	1.120	1.339	1.201, 1.132 1.327, 1.074(N^1)[h]	+0.141, +0.222 −0.181, −0.022[h]	3.24
(**19**)	124.9 (*ca.* 155)	−10.73	−2.28	1.117	1.342	1.153, 1.123 1.341, 1.091	+0.186, +0.234 −0.221, −0.045	6.11
(**20**)	167.6	−9.86	−2.30	1.117	1.352	1.153, 1.131 1.300, 1.154	+0.183, +0.218 −0.102, −0.124	6.69
(**21**)	67.1[f]	−8.67	+1.00[g]	1.141	1.309	1.475, 1.190 1.335(C)	−0.072, +0.088 −0.204	1.25

[a] In kcal mol^{-1}. Corrected values within parentheses. [b] In eV. [c] In Å (1 Å = 100 pm). [d] Electron densities and charges are given in the following order: N^{β}, N^{α}, C^5 and C^1 (or N^1). [e] In debyes. [f] Exptl. value, 71 kcal mol^{-1} (see ref. 15). [g] 'LUMO$_2$'(π_z^*); 'LUMO$_1$'(π_y^*), +0.60 eV. [h] 1.196(N^4) and −0.170(N^4).

might explain the fact that the kinetically favoured isomer is compound (**24**).] Despite the fact that this isomerisation takes place probably through an open intermediate such as (**7e**) or (**7e′**), we have not observed open or cyclised products other than [4 + 2]-cycloadducts under the above mentioned conditions; trapping of diazoazole (**18**), another possible intermediate of this isomerisation if the cycloaddition were reversible, was attempted with phloroglucinol, without success. From another point of view, the fact that both the possible structural isomers (**24**) and (**25**) can be isolated suggests two things: that this may be a common feature in the chemistry of 1,2,4-triazoles when the π-system (rather than the non-bonding nitrogen pairs) is involved and that between the two interpretations afforded by Padwa *et al.*[5] regarding the reactivity of 3-diazo-5-phenyl-3*H*-1,2,4-triazole with 1,1-dimethoxyethene the second one seems more likely.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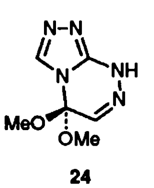
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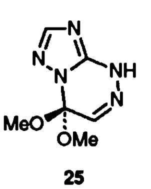
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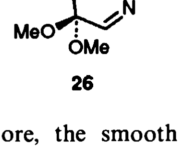
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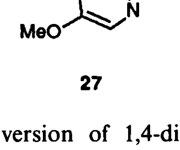
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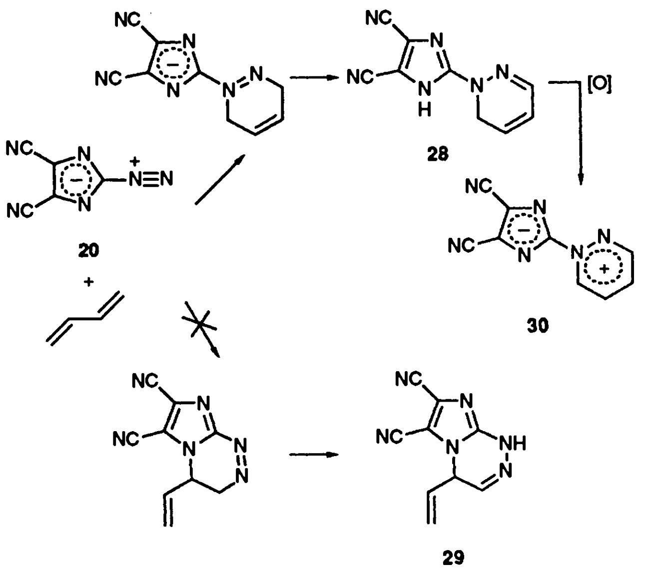
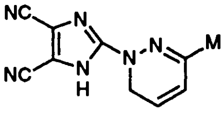
Furthermore, the smooth conversion of 1,4-dihydro-4,4-dimethoxy-7-phenylpyrazolo[5,1-*c*][1,2,4]triazine (**26**) into compound (**27**) by loss of methanol, in chloroform at room temperature, has been demonstrated, as explained in the Experimental section. In dimethyl sulphoxide there was no change within 20 days, unless a drop of trifluoroacetic acid was added, in which case compound (**27**) was rapidly formed. In CD_3OD, compound (**27**) was not formed but the exchange between CH_3O and CD_3O was clearly observed, which confirmed that the reaction is reversible.

Finally, the reaction of α-diazoazoles with butadiene derivatives has been studied again, with the purpose of searching for the conditions and substrates that favour either the formation of azolyldihydropyridazines, which may be considered the normal [4 + 2]-cycloadducts of dienes and N≡N triple bonds, or azolotriazine derivatives, viewed as reverse-electron-demand cycloadducts of an α-diazoazole and



an activated double bond. In the case of compound (**20**), in agreement with the literature,[12,14] only the first type of cycloaddition—*i.e.*, compound (**28**) but not (**29**)—is obtained.

In solution, compound (**28**) is oxidised to the mesomeric betaine (**30**),[23] a known reaction.[24] Starting from compound (**20**) and (*E*)-penta-1,3-diene the result was similar: *N*-(4,5-dicyanoimidazol-2-yl)-1,6-dihydro-3-methylpyridazine (**31**), which also can be readily oxidised to the corresponding betaine (**32**), was isolated as the main product. The reaction also worked with compound (**20**) and 2,3-dimethylbutadiene, as Padwa and Tohidi have shown.[12] However, butadiene, penta-1,3-diene, and 2,3-dimethylbutadiene failed to react with compound (**15**), with compound (**18**) and with 3-diazo-3*H*-indazole. It seems that these dienes are only able to afford cycloadducts by reacting with the most polar diazoazoles.



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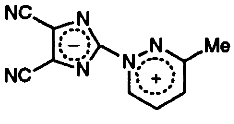

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Experimental

M.p.s were determined on a Büchi apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were obtained on a Varian XL-200 spectrometer; chemical shifts are given in ppm with respect to internal Me_4Si (^1H and ^{13}C), and *J*-values are in hertz. The IR spectra were recorded in KBr on a Perkin-Elmer 681 instrument; only the most significant absorptions (in cm^{-1}) are indicated. Mass spectra were recorded on a Hewlett-Packard 5988A spectrometer.

Reaction of 4,5-*Dicyano*-2-*diazo*-2H-*imidazole with* 1,2-*Dimethoxyethene.*—To a stirred solution of compound (**20**)[12,14] (0.360 g, 2.5 mmol) in anhydrous benzene (25 ml) at 5 °C was added 1,2-dimethoxyethene (mainly the *Z*-isomer)[21] (0.660 g, 7.5 mmol). The resulting yellow solution was maintained at room temperature, in the dark, for 1 h. Evaporation of the solvent gave crude bicycle (**23**) (0.551 g, 95%), which was recrystallised from CH_2Cl_2–hexane to afford a white solid, m.p. 160–162 °C (decomp.), (lit.,[14] 157–157.5 °C); *m/z* 232 (M^+, 31%) and 200 (100); ν_{max} 3300–2800, 2240, 1655 and 1625; $\delta_H[(CD_3)_2SO]$[14] 3.16 (3 H, s), 3.79 (3 H, s) and 6.46 (1 H, s); $\delta_C(CDCl_3)$ 55.5 (q), 56.2 (q), 78.6 (d), 104.5 (s), 108.0 (s), 111.3 (s), 123.0 (s), 145.2 (s) and 146.2 (s).

Reaction of 3-*Diazo*-3H-1,2,4-*triazole with* 1,1-*Dimethoxyethene.*—To a solution of diazo-1,2,4-triazole (**18**) [prepared by diazotisation of 3(5)-amino-1,2,4-triazole (0.84 g, 10 mmol) in a small volume of cold, aq. acid, neutralisation, addition of cold acetone, and drying] in acetone (300 ml) at 0 °C was added 1,1-dimethoxyethene[9] (2.64 g, 30 mmol). The solution was then stirred at room temperature for 2.5 h in the dark. Evaporation of the solvent afforded an orange solid that appeared to be a mixture of isomers (**24**) and (**25**) in a 62:38 ratio, which was separated by 'flash' chromatography (CH_2Cl_2–MeOH mixtures) to afford compound (**24**) (0.900 g, 49%) and compound (**25**) (0.560 g, 31%). Compound (**24**) had m.p. 174–175 °C; *m/z* 183 (M^+, 10%, 152 (65) and 59 (100); ν_{max} 3300–2800, 1640 and 1587; $\delta_H[(CD_3)_2SO]$ 3.19 (6 H, s), 6.94 (1 H, s) and 8.62 (1 H, s); $\delta_C[(CD_3)_2SO]$ 51.4 (q), 99.3 (s), 128.5 (d), 134.4 (d) and 146.9 (s).

Compound (**25**) had m.p. 132–133 °C; *m/z* 183 (M^+, 10%) and 152 (100); ν_{max} 3300–2800, 1637 and 1587; $\delta_H[(CD_3)_2SO]$ 3.18 (6 H, s), 6.89 (1 H, s) and 7.94 (1 H, s); $\delta_C[(CD_3)_2SO]$ 51.6 (q), 99.6 (s), 130.8 (d), 148.8 (s) and 150.4 (d). In D_2O (0.4 ml), after 4 days at room temperature compound (**24**) (20 mg) was completely isomerised to partially *C*-deuteriated (**25**); a few days later on it was shown by NMR spectroscopy that compound (**25**) began to be hydrolysed.

Reaction of 3-*Diazo*-5-*phenyl*-3H-*pyrazole with* 1,1-*Dimethoxyethene.*—To a solution of 3-diazo-5-phenylpyrazole (0.344 g, 2.0 mmol) [prepared by diazotisation of 3(5)-amino-5(3)-phenylpyrazole (0.446 mg, 2.8 mmol), followed by neutralisation and extraction with CH_2Cl_2] in anhydrous MeCN (25 ml) was added 1,1-dimethoxyethene (0.443 g, 5.0 mmol). The mixture was stirred at room temperature in the dark for 12 h. Evaporation under reduced pressure afforded a brown solid (0.5 g), which was purified by crystallisation in CH_2Cl_2–hexane to afford pure 1,4-dihydro-4,4-dimethoxy-7-phenylpyrazolo-[5,1-*c*][1,2,4]triazine (**26**) (0.105 g, 20%), m.p. 146–147 °C; *m/z* 258 (M^+); ν_{max} 3300–2850 and 1570; $\delta_H[(CD_3)_2SO]$ 3.56 (6 H, s), 6.31 (1 H, s), 6.87 (1 H, s), 7.57–7.62 (2 H, m) and 8.03–8.08 (3 H, m); $\delta_C[(CD_3)_2SO]$ 51.6 (q), 86.8 (d), 97.1 (s), 128.3 (d), 139.7 (q), 150.9 (q) [and 125.6 (d), 128.6 (d), 129.9 (d) and 132.6 (s) due to Ph]. Attempts to purify the crude product by column chromatography (silica gel, CH_2Cl_2–MeOH 99:1) caused partial elimination of methanol to give 4-methoxy-7-phenylpyrazolo[5,1-*c*][1,2,4]triazine (**27**). This product has been obtained pure as follows: a solution of compound (**26**) (0.025 g, 0.10 mmol) in $CDCl_3$ (0.4 ml) was maintained at room temperature for 20 days until complete conversion was achieved (as monitored by NMR spectroscopy); elimination of the solvent gave, quantitatively, compound (**27**), m.p. 191–192 °C; *m/z* (CI, NH_3) 227 ($M + 1^+$, 65), 244 ($M + 18^+$, 100); ν_{max} 3080 and 1570; $\delta_H[(CD_3)_2SO]$ 4.34 (6 H, s), 7.49 (3 H, m), 7.72 (1 H, s), 8.10 (2 H, m) and 8.83 (1 H, s); $\delta_C[(CD_3)_2SO]$ 58.3 (q), 93.6 (d), 117.7 (d), 147.2 (s), 153.1 (s), 156.2 (q) [and 126.6 (d), 129.0 (d), 129.7 (d) and 131.5 (s)].

Reaction of 4,5-*Dicyano*-2-*diazo*-2H-*imidazole with Buta*-1,3-*diene.*—To a solution of compound (**20**) (0.288 g, 2 mmol) in benzene (40 ml) at 5 °C was added an excess of cold butadiene (1 ml, 26 mmol). The mixture was stirred in the dark at room temperature for 16 h. The precipitate was filtered off, washed with cold benzene, and dried. *N*-(4,5-Dicyanoimidazol-2-yl)-1,6-dihydropyridazine (**28**) (0.294 g, 74%) was obtained as a solid after recrystallisation from acetone–hexane, m.p. 208–210 °C (decomp.); *m/z* 198 (M^+, 73%) and 67 (100); ν_{max} 3400–3100, 2240, 2230, 1650 and 1590; $\delta_H[(CD_3)_2SO]$[14] 4.42 (2 H, dd, *J* 4.2, 2.1), 6.00 (1 H, ddt, *J* 9.9, 3.4, 2.1), 6.33 (1 H, dtd, *J* 9.9, 4.2, 1.7), and 7.12 (1 H, dd, *J* 3.4, 1.7); $\delta_H[(CD_3)_2SO]$ 42.6 (t), 111.5 (s), 117.2 (d), 129.0 (d), 138.6 (d) and 151.2 (2). In solution the product is slowly oxidised to the mesomeric betaine (**30**), as deduced from the signals that appear in the NMR spectra {*e.g.*, $\delta_H[(CD_3)_2SO]$ 8.64 (2 H, m), 9.64 (1 H, m) and 10.37 (1 H, m)}.

Reaction of 4,5-*Dicyano*-2-*diazo*-2H-*imidazole with* (E)-*Penta*-1,3-*diene.*—To a solution of compound (**20**) (0.354 g, 2.4 mmol) in benzene (25 ml) at room temperature, in the dark, was added (*E*)-penta-1,3-diene (0.249 g, 3.6 mmol). The mixture was stirred for 2 h, the solvent was eliminated under reduced pressure, and the resulting brown solid (0.46 g) was purified by column chromatography (silica gel; CH_2Cl_2) to give pale yellow N-(4,5-dicyanoimidazol-2-yl)-1,6-dihydro-3-methylpyridazine (**31**) (0.319 g, 60%), m.p. 223–226 °C; *m/z* 212 (M^+); ν_{max} 3300–3100, 2260, 2240 and 1620; $\delta_H[(CD_3)_2SO]$ 1.99 (3 H, s), 4.27 (2 H, dd, *J* 4.2, 2.0), 5.97 (1 H, dt, *J* 9.8, 2.0) and 6.35 (1 H, dt, *J* 9.8, 4.2); $\delta_C[(CD_3)_2SO]$ 20.9 (q), 41.7 (t), 111.8 (s), 119.7 (d), 129.6 (d), 146.3 (s), and 151.6 (s). Elution with CH_2Cl_2–MeOH (98:2) afforded 4,5-dicyano-2-phenylimidazole (0.049 g, 10%) and then 4,5-dicyano-2-(3-methylpyridazinium-1-yl)imidazolate (**32**) (0.075 g, 14%) as a greenish yellow solid, m.p. 208–210 °C; *m/z* 210 (M^+); ν_{max} 3080, 2220, 1475 and 1425; δ_H[$(CD_3)_2SO$] 2.80 (3 H, s), 8.52 (2 H, m, J_{AB} 8.2 by irradiating at 10.24 ppm) and 10.24 (1 H, dd, J 5.4, 1.5); δ_C($CDCl_3$ + CD_3OD) 21.8 (q), 113.2 (s), 134.3 (d), 136.4 (d), 140.2 (d) and 164.9 (s).

Conclusions.—The compounds (**6′**), tautomers of intermediates (**6**), are predicted to have total energies lower than their isomers (**3**), (**4**), (**4′**), (**5**), (**5′**), (**7**), (**7′**) and (**7″**), so that, at least under equilibrium conditions, the formation of [4 + 2]-cycloadducts arising from a 1,7-cycloaddition, either concerted or stepwise, could be favoured with regard to other possible pathways. The present calculations suggest that even for diazocyclopentadienes (provided that they do not contain large substituents at positions 1 and 4) the energy of the first [4 + 2]-cycloadduct may be slightly lower than that of the spirane-like [3 + 2]-cycloadduct.

Frontier molecular orbital theory predicts that, kinetically, the reaction of α-diazoazoles with electron-rich alkenes closely resembles a Diels–Alder reaction with reverse electron demand, with an initial approach of the two reagents as in a [4 + 2]-cycloaddition; it is reasonable that only the more nitrogenated diazoazoles or those which contain strongly electron-withdrawing substituents do react in this way with electron-rich alkenes. In sharp contrast, the reaction of diazocyclopentadiene and diazoazoles with electron-deficient alkenes under kinetic control conditions should give [3 + 2]-cycloadducts, which then could be converted into other isomers such as the thermodynamically more stable azolotriazines; it is reasonable that only diazocyclopentadiene, the less nitrogenated diazoazoles, or those diazoazoles which contain electron-donating groups do react with electron-deficient alkenes to afford spiranes as the initial intermediates. These predictions appear to be consistent with our experimental data.

Therefore, assumptions concerning the involvement of transient species other than those mentioned in the above paragraph should be kept to a minimum, especially after the demonstration by both us[9] and Shechter and co-workers[10] that some structures were erroneously attributed in the past, and since some observations reported here point to additional mistakes in the literature.

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