CHEMISTRY LETTERS, pp. 1489-1492, 1980. © The Chemical Society of Japan 1980

2,5-DIAZACYCLOPENTADIENYLIDENE: A STANDARD CARBENE OR A HIGHLY REACTIVE DIRADICAL ?

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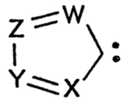
2,5-Diazacyclopentadienylidene (2*H*-imidazolylidene), generated either by photolysis or thermolysis from 2-diazo-2*H*-imidazole, reacts with benzene derivatives to give mainly a mixture of *o*-, *m*-, and *p*-substituted 2-phenylimidazoles. The carbene shows a strong diradical character, in sharp contrast with the well-known behavior of cyclopentadienylidene.

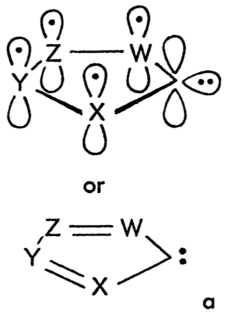
Although the reactivity of cyclopentadienylidenes has been largerly studied during these last fifteen years,[2] very little is known about the chemistry of their aza analogs. In fact, there are ten possible carbenes of type **1**, which could be generated in practice from (aza)diazocyclopentadienes (i.e., from diazocyclopentadiene to diazotetrazole) by thermal or photochemical nitrogen elimination, but beside the parent compound only 3*H*-pyrazolylidene[3] and tetrazolylidene[4] have been studied in detail.



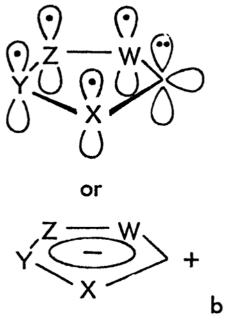
1

X, Y, Z, W = CH or N

For several years we have been interested in diazoazoles because they offer a great deal of synthetic possibilities in the heterocyclic chemistry field,[5] and because their decomposition, conveniently operated, may result in a new entry to fluoroazoles[6] which would no longer require the aqueous medium currently used.[7] With these goals in mind, we have undertaken both an experimental and theoretical study on the nature of (aza)cyclopentadienylidenes (**1**).[8] In short, it can be asked whether the reactivity of these intermediates resembles more that of a conventional carbene (**a**), a peculiar zwitterion (**b**),[9] or a diradical either in the singlet (**c**) or triplet (**d**) state (a simplified picture of the atomic orbitals and electrons presumably involved could be as shown).



a



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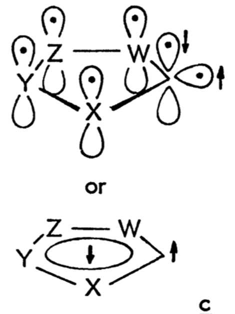

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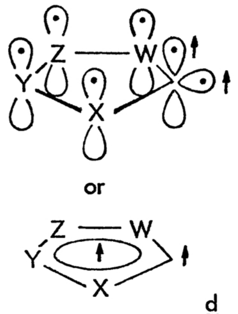
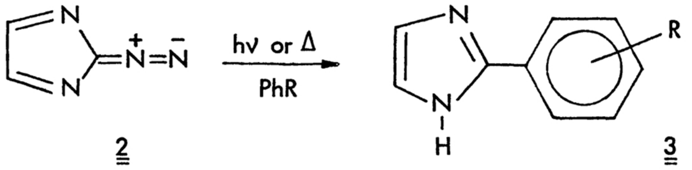


d

In this communication we wish to report our studies on 2*H*-imidazolylidene, a previously unknown carbene which we generated either by photolysis or by heating of 2-diazo-2*H*-imidazole (**2**). Its reactivity towards benzene derivatives was investigated.

The general method followed by us employed diazotisation at -10° of 2-aminoimidazole sulphate (1.32 g) in a small volume of aq. H_2SO_4, carefully neutralisation in cold, addition to a well stirred 200-250 ml of PhR, desication with anh. Na_2SO_4, filtration through anh. $MgSO_4$, degassing of the solutions, and photolysis (Philips HPK-125W lamps, Pyrex filter) at 0-10° for 3-5 hours, or heating (slow addition of organic solutions of **2** into 100 ml of the same refluxing solvent). The residues obtained by elimination of the solvent *in vacuo* were straightforward analysed by TLC, GC, and/or ^{1}H-NMR, and compared in most cases with synthesised authentic samples of 2-[(*o*-, *m*-, and *p*-substituted)phenyl]imidazoles (**3**), the major products of the reaction; then the residues were taken up with dil. aq. HCl, non-basic materials extracted with CH_2Cl_2, and the aq. solutions basified and extracted with CH_2Cl_2 to give solvent- and polymer-free products, which were again analysed by GC and NMR, and/or separated by column chromatography, weighted, and analysed when necessary. The main results are summarised below:



2 **3**

	hν		hν in PhR-PhH[d]		hν (PhCOPh)[e]		Δ	
	overall yield(%)[a]	*o/m/p* ratio	*o/m/p*/H ratio	*o/m/p*/H rel. react.	overall yield(%)[a]	*o/m/p* ratio	overall yield(%)[a]	*o/m/p* ratio
R = OMe	44	58: 9:33	53:8:30:9	18:3:20:1	36	66: 7:27	42	34:16:50
R = Me	70	60:0?:40[b]	37:0?:25:38	3:0:4:1	52	71:0?:29	63	55:0?:45
R = Cl	46	64: 6:30	36:4:16:44	2.5:0.3:2.2:1	45	58:12:30	40	50:10:40
R = NO_2	34	18:54:28[c]	5:29:9:57	0.3:1.8:0.9:1	20	14:53:33	20	30:32:38

[a] Total net amount of imidazole-containing compounds. Yields from the amine.

[b] The *meta* compound was not detected by GC in the crude product, nor by ^{1}H- and ^{13}C-NMR in the main column fractions. However, small amounts of this product can not be excluded in view of the very close physical properties of such *meta* and *para* compounds.

[c] Irradiation of **2** in pyridine gave similar results, with an $\alpha/\beta/\gamma$ ratio equal to 22:66:12.

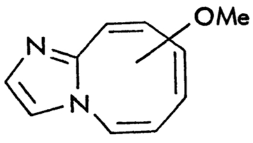
[d] Equimolar mixtures of benzene and substituted benzene.

[e] Solutions *ca.* 0.03 *M* in **2** and 0.2 *M* in PhCOPh externally irradiated with 360 nm light.

From these results some conclusions can be derived: i) the *o*/*m*/*p* ratios obtained in the non-sensitised photochemical experiments agree with the electron-donating or withdrawing character of the substituents, the generated carbene appearing to be of electrophilic nature; ii) the partial rate factors (irradiation in PhR-PhH) indicate that such a carbene is very poorly selective,[10] except for the R = OMe case; iii) the results from the direct and sensitised irradiations do not practically differ, so the electronic configuration of the carbene which arises from the direct photolysis must be close to that of the triplet (such a carbene must have some features of a diradical);[11] and iv) when the carbene is produced by heating, the *o*/*m*/*p* ratios undergo slight variations, which might be speculatively attributed to several factors,[12] but the differences are not important enough (except perhaps for the NO_2 case) to suggest that an "unlike" carbene is operating or an opposite mechanism takes place.

Minor compounds were also produced in some cases. Thus, the gas chromatogram of the irradiation product in anisole showed, beside *o*-, *m*-, and *p*-OMe derivatives, two more volatile compounds (12 and 5%, respectively, of the total amount), to which structure 4 (imidazo[1,2-*a*]azocines) may be attributed on the basis of ^{1}H-NMR and mass spectra; photosensitised irradiation gave smaller amounts of these compounds, whereas in the thermolysis experiment the yields went up to 18 and 16%, respectively. In chlorobenzene as the solvent, a 3-4% yield of a relatively volatile compound was detected (GC), both in the direct photolysis and in the thermal reaction.

Other mechanistically interesting experiments to be reported are: i) photolysis of 2 in benzene gave 65% net overall yield of 2-phenylimidazole, no other simple nitrogen-containing products being isolated; attempts to trap the possible intermediate 5a were unsuccessful; ii) photolysis of 2 in *o*-xylene gave in good yield a mixture of 2-(2,3-dimethylphenyl)imidazole, 2-(3,4-dimethylphenyl)imidazole, and 2-(*o*-tolylmethyl)imidazole in a 42:35:23 ratio; there seems unlikely that the last compound arises from [2+1]-cycloadduct like 5a; and iii) irradiation of 2 in cyclohexene gave small amounts of 2-(1-cyclohexenyl)imidazole and 2-(2-cyclohexenyl)imidazole as the only nitrogen-containing non-polymeric compounds; the [2+1]-cycloaddition compound was not obtained.



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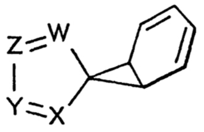
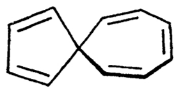


5a, X=W=N
b, all CH



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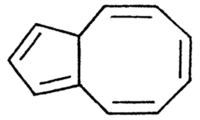

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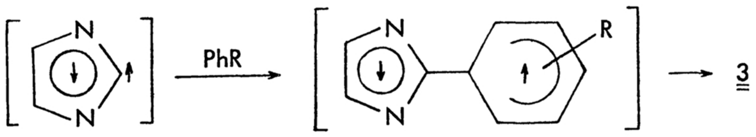
It should be pointed out that all these results differ greatly from those reported for cyclopentadienylidene,[2] in which spironorcaradiene structures (5b) are mainly obtained. Valence tautomeric equilibria (5b ⇌ 6) are afterwards demonstrated in several cases.[2] Furthermore, heating of 5b in benzene gives bicyclo[6.3.0]undecapentaenes (7 and/or related isomers) as the major products.[13]

Obviously, different (aza)cyclopentadienylidenic carbenes can react by different mechanisms, but we think that all the known results can be rationalised on the basis of the relative standard carbene (a) or diradical (c) character of the chemical species involved. In our case, we postulate a mechanism with participation of a highly reactive carbene with a strong diradical character (and with a very electrophilic carbon atom, because it lies between both nitrogens), which passes through 8 as an intermediate. The minor compounds (4) could arise either from 5a[14] or even, although it seems less probable, from a quick disrotatory opening of tricyclic intermediate 9.



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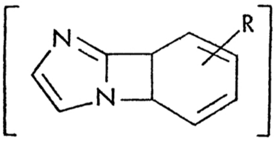

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Acknowledgements. We thank Ms. B. Vallverdú for her assistance in two of the above mentioned experiments and Dr. M. Vuilhorgne for ^{13}C-NMR spectra.

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2. For a recent review, see A. P. Krapcho, Synthesis, 77 (1978). See also "Carbenes", vol. 2, R. A. Moss and M. Jones, Eds., Wiley, New York, 1975.
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4. S. F. Dyer and P. B. Shevlin, J. Am. Chem. Soc., 101, 1303 (1979).
5. For a good, comprehensive review on the subject, see M. Tisler and B. Stanovnik, Heterocycles, 4, 1115 (1976).
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7. K. L. Kirk and L. A. Cohen, J. Am. Chem. Soc., 95, 4619 (1973).
8. In order to ensure that the observed features are properly attributed to the heterocyclic carbene electronic configuration, ring substituents such as phenyl and, of course, strong electron-donating or withdrawing groups must be avoided, even though their exclusion implies greater experimental difficulties concerning the isolation and stability of diazoazoles.
9. Configuration b (related to the S_2 excited state) may be electronically compared to the species resulting when nitrogen is evolved from a diazonium salt.
10. Statements i and ii, both together, may suggest that an electrophilic radical is formed. See, for instance, R. Ito, T. Migita, N. M. Morikawa, and O. Simamura, Bull. Chem. Soc. Japan, 36, 992 (1963), and ref. therein. For a review, see D. H. Hey, Bull. Soc. Chim. Fr., 1591 (1968).
11. An alternative explanation might be that the triplet carbene is formed in both cases, but it seems rather unlikely.
12. For instance, to changes in the steric hindrance and/or in the solvent molecules mobility.
13. D. Schonleber, Chem. Ber., 102, 1789 (1969).
14. Generated either from 8 or directly from 1 (X=W=N) in a concerted process.

(Received May 6, 1980)