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NITROVINYLCARBENES : PHOTOLYSIS OF THE 3H-PYRAZOLE PRECURSORS, INTRAMOLECULAR EVOLUTION AND INTERMOLECULAR REACTIVITY.

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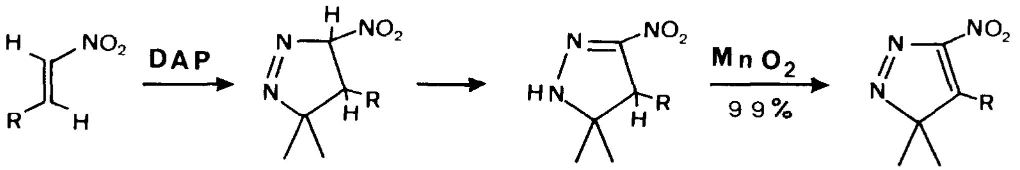
The photolysis of different nitro 3H-pyrazoles, obtained indirectly from nitroethylenes, is studied. Inter and intramolecular processes to stabilization are observed with conservation of the nitro group in the case of an α-nitro vinylcarbene. On the contrary the β-nitrocarbene reacts to give α-oximinoketones.

The cyclization of acyclic vinyl carbenes to cyclopropenes is considered to be their most common reaction (1). However this intramolecular process is not always observed and a number of intermolecular cycloaddition reactions has been reported in the case of various substituted isoprenic vinylcarbenes (2). The unusual situation encountered with a sulfinyl substituent, where the cyclopropene derivative is in equilibrium with the vinylcarbene (3), prompted us to extend our study to other heteroatomic substituents with a semi-polar bond. We report here our results dealing with nitrocarbenes, a particularly interesting case owing to the scarcity of such species. The previous studies of U. Schöllkopf et al. (4) showed that nitrocarbenes are elusive intermediates which could not be trapped as such, but lead exlusively to radical fragmentation and decomposition products.

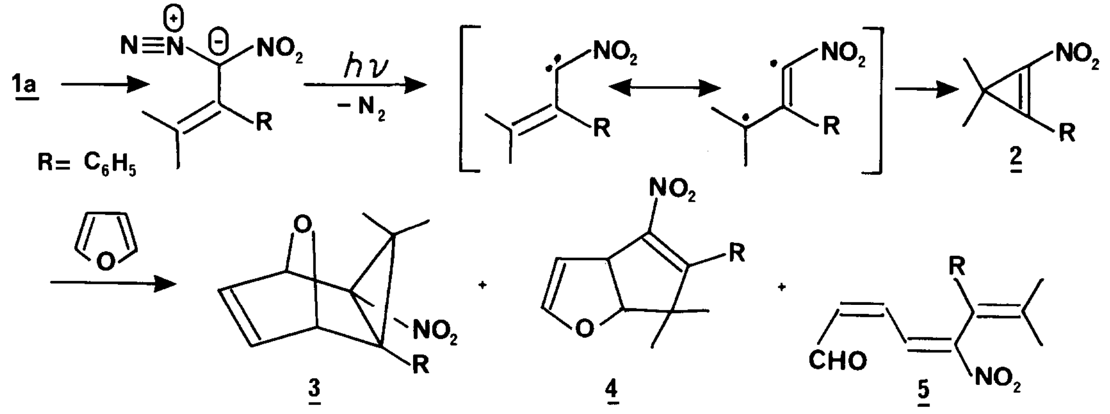
The usual way to produce vinylcarbenes is by photolysis of 3H-pyrazoles. These precursors are usually obtained by 1,3-dipolar cycloaddition of disubstituted diazoalkanes to electrophilic acetylenes (5). However nitroacetylenes have received little attention in the literature, being potentially explosive (6). We employed therefore an indirect synthetis of 5-nitro 3H-pyrazoles. This was most conveniently achieved by dehydrogenation with manganese dioxide of the corresponding Δ^2-pyrazolines, easily obtained by cycloaddition of 2-diazopropane (DAP) to the more common nitroethylenes (7) :



a R = C_6H_5 b R = CN

1a , 1b

Photolysis of both 3H-pyrazoles 1a and 1b in relatively inert solvents such as methylene chloride or ether leads to nearly quantitative evolution of nitrogen, but no major products could be isolated or characterized from the complex irradiation mixtures. The situation is not improved by use of unsaturated solvents such a vinylic ethers for the 3H-pyrazole 1b, the photolysis, monitored by the N_2 evolution being rapidly blocked by the formation of coloured polymeric materials. In contrast the photolysis of the 3H-pyrazole 1a in furan (8) leads to considerable N_2 evolution (85 % of stoichiometry) along with pronounced colour changes (yellow → violet → pale brown). From the irradiation mixture, apart from nearly 50 % of insoluble polymer- like material, four compounds can be isolated by careful liquid chromatography over SiO_2 (Hexane with 5-20 % ether).



3 : colourless crystals m.p. = 63°C ; IR : $\nu(NO_2)$ 1525 and 1350 cm^{-1} ; NMR : δ = 1.22 (3H,s) 1.78 (3H,s) 4.86 (1H,broad s) 5.47 (1H,broad s) 6.72 (1H,m) and 6.88-7.44 (6H,m)

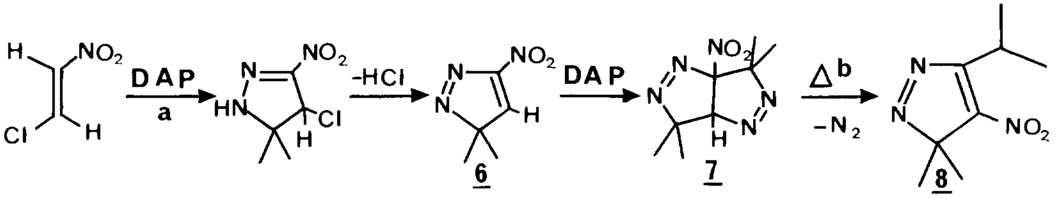
4 : colourless crystals m.p. = 95-96°C ; IR : $\nu(NO_2)$ 1540 and 1365 cm^{-1} ; NMR : δ = 1.07 (3H,s) 1.54 (3H,s) 3.45 (1H,dd,J = 3Hz and 4.5 Hz) 4.64 (1H,t,J = 3 Hz) 5.24 (1H,d J = 4.5 Hz) 6.46 (1H,d,J = 3 Hz) and 7.22-7.50 (5H,m)

5 : Yellow liquid ; IR : $\nu(NO_2)$ 1525 and 1330 cm^{-1}, $\nu(C=O)$ 1675 cm^{-1} ; UV : λmax. = 238 nm (17000) Sh. = 280 nm (11500) and 365 nm (2400) ; NMR : δ = 1.82 (3H,s) 1.92 (3H,s) 6.30 (1H,d d,J = 7 Hz and 11 Hz) 7.06 (1H,t,J ≃ 12 Hz) 8.43 (1H,d,J = 12.5 Hz) 10.32 (1H,d,J = 7 Hz) and 7.15-7.60 (5H,m).

The most polar of these is the recovered starting material 1a (15 %). The other compounds 3, 4 and 5 are all isomeric products bearing a nitro group. The major species 3, isolated in 22 % yield, is the Diels-Alder adduct of furan with the intermediate cyclopropene 2 formed by intramolecular cyclization of the vinylcarbene (9). Compound 4, isolated in 11 % yield appears to be an intermolecular addition product of the 1,3 delocalized form of the vinylcarbene (10). Compound 5, isolated in 8 % yield is a highly unsaturated aldehyde which can either be formed directly from furan and the carbene, most probably via the triplet state, or through furanocyclopropanic rearrangement from a non isolated intermediate cyclopropane (11). The ratio of intermolecular/intramolecular reaction of the vinylcarbene is therefore at least 0.9 : 1 (total yield 41 %). An irradiation experiment stopped after

40 % N_2 evolution shows that polymer formation is reduced, the products 3, 4 and 5 now being isolated in 25 %, 15 % and 22 % yield, based on the amount of effectively decomposed 3H-pyrazole (Inter/intra ≃ 1.5 : 1). The control photolysis of the isolated compounds 3, 4 and 5 in furan (i.e. under the conditions of their formation) shows that only the Diels-Alder adduct 3 is photostable, 4 and 5 being rapidly transformed into unidentified products, whose NMR spectra are similar to those of the previously mentioned polymers. The intermolecular reaction rate of this nitrovinylcarbene toward furan is in consequence greater than the cyclisation rate. To our knowledge, this is an unusual case where a nitrocarbene leads to the formation of well defined adducts with conservation of the nitro function, instead of radical fragmentation products. This probably results from additional stabilization of the carbene by electronic delocalization over both the nucleophilic vinyl group and the strongly electrophilic nitro group.

The C4-unsubstituted 3H-pyrazole 6 cannot be reached by MnO_2 dehydrogenation (7). We attempted therefore its preparation starting from chloronitroethylene with subsequent dehydrohalogenation (12). Fortunately this is easy to achieve, employing excess 2-diazopropane as base, but a second 1,3-dipolar cycloaddition occurs, yielding the bis Δ^1-pyrazoline 7, isolated in 76 % yield from chloronitroethylene :

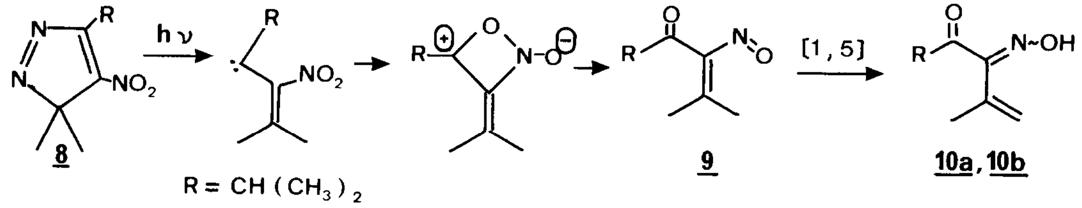


a 7 equiv. DAP ; ether : -60°C 0°C b toluene : 90° C ; 1 h

7 : colourless crystals m.p. = 86°C, isolated by recrystalization in hexane-ether at -78°C ; IR : $\nu(NO_2)$ 1550 and 1375 cm^{-1} ; UV : λmax 256 nm (1550) and 325 nm (480) ; NMR : δ = 1.46 (3H,s) 1.50 (3H,s) 1.64 (3H,s) 1.71 (3H,s) and 5.40 (1H,s)

8 : yellow crystals m.p. = 46°C, isolated in 75 % yield by chromatography on SiO_2 (hexane/ether 9 : 1) ; IR : $\nu(NO_2)$ 1515 and 1360 cm^{-1} , (C=C-N=N) 1640 cm^{-1} ; UV : λmax 280 nm (6900) ; NMR : δ = 1.44 (6H,d,J = 7 Hz) 1.65 (6H,s) and 3.78 (1H, hept.,J = 7 Hz).

Heating this bis-adduct to 90° C in toluene induces only the extrusion of the azo part adjacent to the electronattracting substituent. This leads to the 3H-pyrazole 8, a precursor of a β-nitrovinylcarbene probably not obtainable directly by a 1,3-dipolar cycloaddition. On photolysis in methylene chloride, 90 % of the stoichiometric nitrogen content is rapidly evolved. The irradiation product, apart from 10 % recovered pyrazole 8, is composed of a mixture of the isomeric oximes 10a and 10b, slightly contamined by another isomeric violet compound, which is probably the intermediate nitrosoderivative which converts slowly into 10b.



8

R = CH(CH$_3$)$_2$

9

10a, 10b

10a/10b : formed nearly quantitatively (NMR), separated by SiO$_2$ chromatography (hexane/ ether 4 : 1)

10a : colourless crystals, m.p. = 56°C isolated pure 37 % ; IR : ν(OH) 3560 cm^{-1} (fine) 3300 cm^{-1} (broad), ν(C=O) or ν(C=N) 1690 cm^{-1} ; NMR : 1.13 (6H,d,J = 7 Hz) 1.91 (3H,broad s) 3.51 (1H,hept.,J = 7 Hz) 4.92 (1H,broad s) 5.34 (1H,broad s) and 8.63 (1H,broad s)

10b : pale yellow liquid, isolated pure 13 % ; IR : ν(OH) 3580 cm^{-1} (fine), 3300 cm^{-1} (broad), ν(C=O) or ν(C=N) 1705 cm^{-1} ; NMR : δ = 1.17 (6H,d,J = 7 Hz) 1.94 (3H, broad s) 2.86 (1H,hept.,J = 7 Hz) 5.06 (1H,broad s) 5.38 (1H,broad s) and 8.84 (1H,broad s).

The formation of these compounds is best rationalized by an intramolecular oxygen transfer from the nitro group to the carbenic center, followed by a [1,5]H-shift. The oxido-reductive step is then mechanistically analogous to the nitro- to nitrito-carbene rearrangement proposed by Schöllkopf for α-nitrocarbenes, however with the important difference that stable compounds result here.

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The indicated yields are for products which gave satisfactory microanalyses, IR (CHCl$_3$), UV (λmax (ε) in CH$_3$CN) and NMR (CDCl$_3$/TMS) spectra.

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8.) Medium pressure lam Philips HPK 125 ; Pyrex glass filter ; 0.5 % solution in furan ; 15°C ; under Argon.
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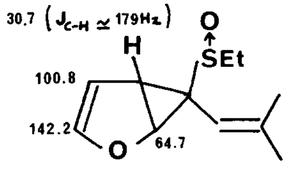
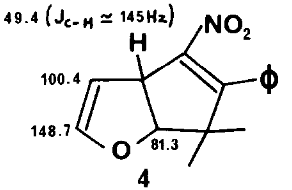
10.) As suggested by a referee, a furanocyclopropane structure seems unlikely on the basis of the spectroscopic data of this adduct. Additional evidence for structure 4 comes from the thermal stability (no transformation observed by heating at 70°C (11)) and by comparison with ^{13}C NMR data of related compounds:





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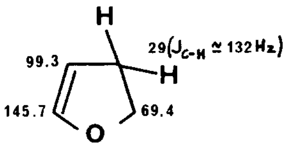

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