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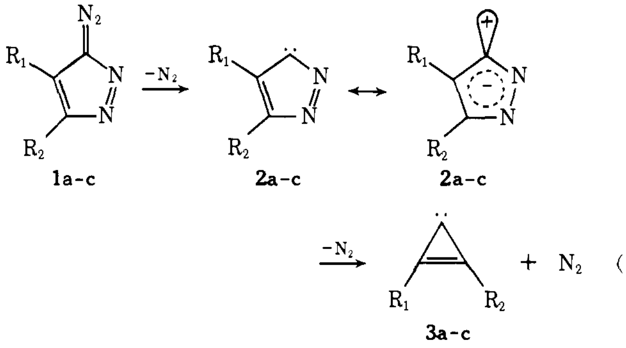
3-Diazopyrazoles: Sources of Unusual Carbenes and Dipolar Reagents

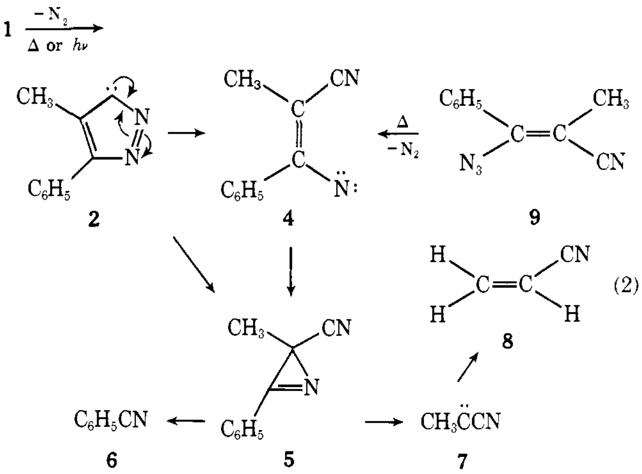
Sir:

Knowledge of the carbenic chemistry of 3-diazopyrazoles[1a] is limited to photolytic conversions of 3-benzoyl-5-diazo-4-phenylpyrazole in aqueous acetone and in benzene to 3(5)-benzoyl-4-phenylpyrazole and 3-benzoyl-4,5-diphenylpyrazole, respectively. There is no information relative to 3-diazopyrazoles as dipolar reagents.[1b] A study is presently summarized of decomposition and dipolar reactions of 3-diazopyrazoles **1a–c** and novel behavior of 3*H*-pyrazolylidenes **2a–c.** Carbenes **2a–c** might be expected to behave as highly electrophilic singlets and as possible sources of cyclopropenylidenes **3a–c** (eq 1).[1c] It has now been observed that 3*H*-pyrazolylidenes (a) isomerize to 2*H*-azirines (eq 2), (b) are capturable prior to carbenic rearrangement by insertion into C–H bonds (eq 3), (c) react with benzene by substitution and by ring expansion/sigmatropic rearrangement processes (eq 4 and 5), and (d) cleave ethers by nucleophilic attack on oxygen to give 1,2- and 1,3-adducts (eq 6). Of further note is that 3-diazopyrazoles undergo dipolar reactions with electron-rich olefins to yield 1,4- instead of 1,3-adducts (eq 7).



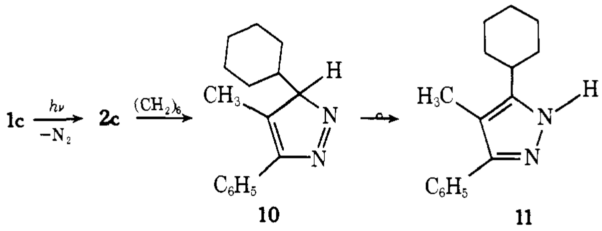
3a-c
(1)

3-*tert*-Butyl-5-diazopyrazole (**1a**), 3-diazo-5-phenylpyrazole (**1b**), and 3-diazo-4-methyl-5-phenylpyrazole (**1c**), prepared by diazotization of the corresponding amines[2a–c] with nitrous acid in fluoboric or hydrochloric acids and neutralization with aqueous carbonates, are sensitive solids but, with care, are easily manipulated.[2d] Pyrolysis of **1c** at 250 °C (60 mmHg) yields 2-cyano-2-methyl-3-phenyl-2*H*-azirine (**5,** > 60%),[3a,b] benzonitrile (**6,** 10%), and acrylonitrile (**8**). Photolysis of **1c**[3c] in cyclohexane also gives **5** (competitive solvent insertion is to be subsequently discussed). There was no evidence for cyclopropenylidene **3c** in these experiments. The structure of **5** is established from its spectra[3b] and by comparison with an identical product obtained by thermolysis of *β*-azido-*α*-methylcinnamonitrile (**9**).[3d] Conversion of **1c** to **5** possibly occurs by ring-opening of **2c** to nitrene **4** and subsequent heterocyclization or/and by concerted rearrangement of **2d.** Fragmentation products **6** and **8** may result from carbenic collapse of **5** (eq 2) and hydrogen migration in the methylcyanocarbene (**7**) generated.[4] At 175–300 °C (>50 mmHg) **1a** and **1b** yield 3-*tert*-butyl-2-cyano-2*H*-azirine (>35%)[5a] and 2-cyano-3-phenyl-2*H*-azirine (65%),[5b] respectively. Decomposition of 3-diazopyrazoles to 2*H*-azirines appears to be general and of value synthetically.

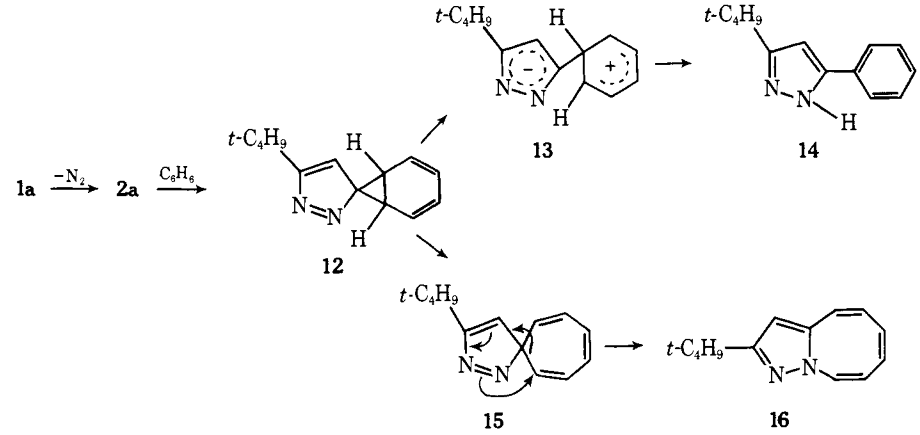


(2)

Irradiation of **1c**[3c] in cyclohexane yields 3(5)-cyclohexyl-4-methyl-5(3)-phenylpyrazole[3a,6a] (**11,** 60%; eq 3) and azirine **5** (15%). Along with generation of **5** photolytically, this experiment reveals that **2c,** apparently a discrete intermediate, inserts into cyclohexane to give **11,** presumably after 1,5-sigmatropic isomerization of **10.** Pyrazolylidene **2a,** produced thermally or photolytically[3c] from **1a,** reacts with benzene to yield 3(5)-*tert*-butyl-5(3)-phenylpyrazole[3a,6b] (**14,** 85–90%) and 2-*tert*-butylpyrazolo[3,2-*a*]azocine[3a,6c] (**16,** 10%), a derivative of a new heterocyclic system. Formation of pyrazole **14** and azocine **16,** assigned from their analyses and spectra, is rationalized by eq 4 and 5 and is formally analogous to photolytic conversion of 5-diazo-1,2,3-triphenyl-1,3-cyclopentadiene in benzene[6d] to 1,2,3,4-tetraphenyl-1,3-cyclopentadiene and 9,10,11-triphenyl-2,4,6,8,10-bicyclo[6.3.0]undecapentaene. The transformation of significance is the apparent 1,5-sigmatropic[6e] rearrangement of **15** as led by pyrazolo nitrogen rather than carbon, and, on the basis of the mechanistic aspects of eq 4 and 5, reactions of **1a** with benzenes containing electron-withdrawing substituents are predicted to give increased conversions to pyrazolo[3,2-*a*]azocines.



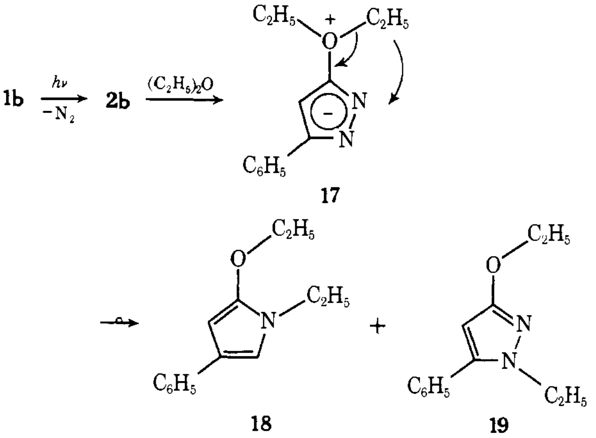
(3)



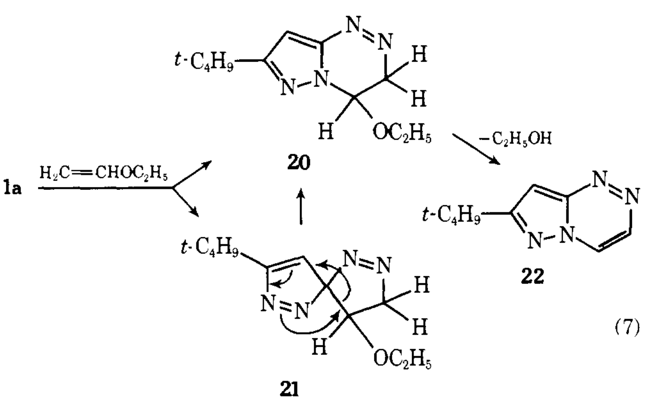
(4)

(5)

3-Diazopyrazoles react with nucleophiles. Pyrrolidine adds (~100%) to **1c** at 0 °C with hydrogen migration to form 3(5)-phenyl-5(3)-(1-pyrrolidinylazo)pyrazole.[3a,7a] Methanol at 65 °C decomposes **1a** with loss of nitrogen to yield 3(5)-*tert*-butylpyrazole (42%)[7b] and 3(5)-*tert*-butyl-5(3)-methoxypyrazole (39%).[3a,7c] Of particular interest is that photolysis of **1b** in ethyl ether results in cleavage (~80%) of the ether yielding 5-ethoxy-1-ethyl-3-phenylpyrazole[3a,8] (**18**) and 3-ethoxy-1-ethyl-5-phenylpyrazole[8] (**19**) in 3:2 ratio. Carbenes have been reported to rupture ethers at oxygen to give 1,1-derivatives.[9] The present conversion of ethyl ether differs, however, in that the carbenic derivatives are formal 1,2- and 1,3-adducts. Attack at ether oxygen implies that **2b** functions as an electrophilic singlet (eq 6) and then oxonium ylide **17** converts to **18** and **19**. Isomerization of **17** to **19** does not occur, however, by successive 1,5-sigmatropic rearrangements because **18** is stable under the conditions of its formation. Conversion of **17** to **18** and **19** is speculated to take place by ionization-recombination or by bimolecular processes.



(6)



(7)

Diazopyrazole **1a** adds to electron-rich olefins. Thus ethyl vinyl ether and **1a** undergo cycloaddition at 0 °C with elimination of ethanol to give 7-*tert*-butylpyrazolo[3,2-*c*]-*as*-triazine (**22**, ~100%).[3a,10] It is not known whether **1a** reacts by direct 1,4-cycloaddition to form **20** or by 1,3-cycloaddition to yield **21** and then 1,5-rearrangement as in eq 7. It is clear, however, that 3-diazopyrazoles are versatile reagents for polar heterocycloaddition as well as sources of unusual carbenes. Further elaboration of the chemistry of 3*H*-pyrazolylidenes and 3-diazopyrazoles is in progress.

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References and Notes

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(5) (a) Spectra: IR: 2220 ($C{\equiv}N$) and 1770 ($C{=}N$) cm^{-1}; NMR ($CDCl_3$) δ 1.33 (s, 9, $C(CH_3)_3$) and 2.20 (s, 1, –CH–). (b) IR: 2220 ($C{\equiv}N$) and 1760 ($C{=}N$) cm^{-1}; NMR ($CDCl_3$) δ 2.6 (s, 1, H), 7.70 (m, 3, C_6H_5), and 7.9 (m, 2, C_6H_5).

(6) (a) Mp 175–176 °C. (b) Mp 119–120 °C; IR 3160 cm^{-1} (NH); NMR ($CDCl_3$) δ 1.35 (s, 9, $C(CH_3)_3$), 6.30 (s, 1, 4-pyrazolo H), 7.28 (m, 3, C_6H_5), and 7.65 (m, 2, C_6H_5). Dimethyl sulfate converts **14** (~100%) to 3-*tert*-butyl-1-methyl-5-phenylpyrazole. (c) Mp 56–57 °C; IR 2990, 1670, 1460, 1370, 810, and 690 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (s, 9, $C(CH_3)_3$), 5.90 (m, **4**, H at C-3,4,5,6), 5.93 (s, 1, **4**-pyrazolo H), 6.25 (d, 1, H at C-2, J = 10.5 Hz), and 6.67 (d, 1, H at C-7, J = 9.5 Hz); UV (C_6H_{12}) λ_{max} 230 (ϵ 13 000) and 280 (ϵ 6700). The NMR of the azocine ring protons of **16** is similar to that of the cyclooctatriene moiety of 9,10,11-triphenyl-2,4,6,8,10-bicyclo[6.3.0] undecapentaene. (d) H. Dürr and G. Scheppers, *Chem. Ber.*, **103**, 380 (1970). (e) 1,7-Rearrangements (H. Dürr, H. Kober, I. Halberstadt, U. Neu, T. T. Coburn, T. Mitsuhashi, and W. M. Jones, *J. Am. Chem. Soc.*, **95**, 3818 (1973)) are not observed in the present system.

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(10) Yellow needles, mp 135–136 °C, NMR ($CDCl_3$) δ 1.45 (s, 9, $C(CH_3)_3$), 7.1 (s, 1, H), 8.58 (d, 1, H, J = 5 Hz), and 8.8 (d, 1, H, J = 5 Hz).

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