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PYRIDAZINO[2,3-b]BENZO-1,2,4-TRIAZINE. A NEW HETEROCYCLE AND A NEW STABLE FREE RADICAL

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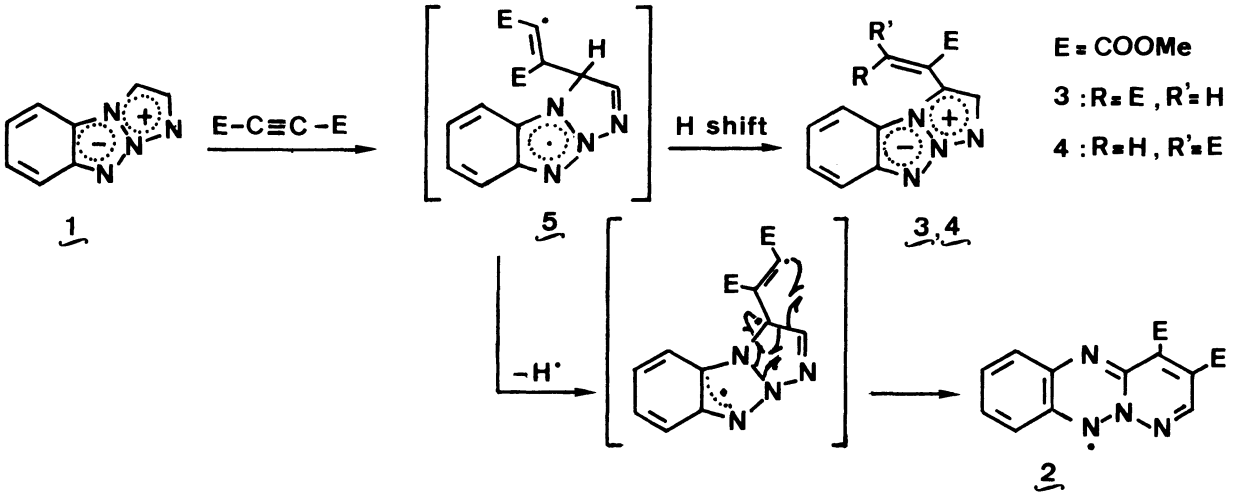
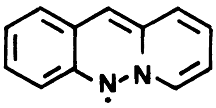
The preparation of the new stable free radical 2,a derivative of the previously unreported pyridazino[1,2-b]benzo-1,2,4-triazine, and some of its chemical properties are described.

In the frame of our study of the chemistry of heteropentalenes, a class of mesomeric betaines of remarkable stability,1,2) we investigated the reaction of some pyrazolo and triazolo benzotriazoles with dimethyl acetylenedicarboxylate (DMAD) and found that cycloaddition or Michael-type addition to form new heteropentalenes are usually the main processes. However, the reaction of triazolo[1,2-a] benzotriazole (1)3) takes a different course as will be reported in the following. Thus 1 reacts with one equivalent of DMAD in refluxing toluene to give only minor amounts of the Michael adducts 3 and 4 while the main product (20-37% isolated yield) is a dark blue crystalline material.4) According to the mass spectrum this product results from the addition of one mole of DMAD and the loss of one hydrogen atom. That this compound is a free radical is supported by the deep colour and the presence of a ESR signal, and has been finally confirmed by a x-ray analysis, revealing the structure of dimethyl pyridazino[2,3-b]benzo-1,2,4-triazine-3,4-dicarboxylate radical (2), the first reported derivative of this heterocycle.5) This compound can be understood as arising from the same intermediate 5 intervening also in the Michael addition, with the difference that a hydrogen is lost rather than shifted, and a series of rearrangements takes place at the radical stage until the stable configuration 2 is reached.





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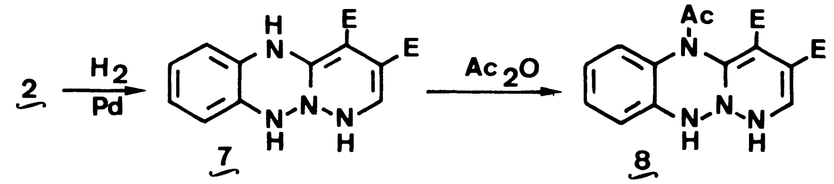

Compound 2 establishes a new class of stable free radicals, the prototype of which would be pyrido[1,2-b]cinnoline radical.[6)]

The exceptional stability of free radical 2, a 15π electron system,[5)] is shown by the following evidences. Thus, crystalline samples were found unchanged after a year, and even dilute air equilibrated solutions can be kept without substantial decomposition for at least one week at room temperature. The stability as well as the relatively easy availability[4)] of this free radical makes it attractive as ESR standard. Cyclic voltammetry shows reversible oxidation, strictly monoelectronic as checked by coulometric measurements (0.98 ± 0.02 equiv.), yielding the stable yellow cation, a 14π electron system. Catalytic reduction (1 atm, 20 °C, ethanolic solution in the presence of 10% Pd on charcoal) takes place with absorption of 1,5 mole equivalents of hydrogen to give a yellow fluorescing solid which is recognized as dimethyl 5,10-dihyropyridazino[2,3-b]benzo-1,2,4-triazine-3, 4-dicarboxylate (7), and accordingly shows three separate N-H bands in the solution IR spectrum.[7)] Compound 7 gives a monoacetyl derivative 8, in accord with the presence of only one "aminic" NH.[7)]

Further study of the chemistry of free radical 2 and related heterocyclics is in progress. The Ministry of Education is thanked for supporting this work.

References

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2)For a review on heteropentalenes, see C.A.Ramsden, Tetrahedron, 33, 3203 (1977).

3)J.C. Kauer and R.A. Carboni, J. Am.Chem.Soc., 89, 2633 (1967).

4)Chromatographic separation affords 2, 3,and 4 in 37, 4, and 4% yields respectively. However, a 20% yield of pure 2 is obtained by direct crystallization from the toluene mother solution.

5)Crystallographyc data: monoclinic crystals a = 9.222(7), b = 15.335(10), c = = 9.544(2) Å; Space group $P\ 2_1/c$; final R-factor = 0.040 for 590 reflections. (Dr. B. Bovio). The well resolved ESR spectrum in benzene satisfyingly correlates with MO calculation for a π radical (Dr. A. Faucitano). We thank our colleagues for these data, which will be the subject of separate communications.

6)Only some mesoionic derivatives of pyrido[1,2-b]cinnoline were reported, R.Y. Ning, W.Y. Chen, and L.H. Sternbach, J. Heterocycl. Chem., 11, 125 (1974).

7)All new compounds gave correct analytical data. Mass spectral fragmentations are in accord with their structures. Product 2: mp 215-217 °C; no fine structure NMR spectrum due to the paramagnetism; ν(Nujol) 1720, 1560, 1510 cm^{-1}. Product 7: mp 169-170 °C; δ($CDCl_3$-CF_3COOD) 4.2 (s,6H), 7,8 (br,s,4H), 9.3 (s,1H); ν($CHCl_3$) 3460, 3415, 3360 cm^{-1}; ν(Nujol) 1700, 1635, 1580 cm^{-1}. Product 8: mp 220-221 °C; δ($CDCl_3$) 2.4 (s,3H), 3.6 (s,3H), 3.8 (s,3H), 6.5-6.9 (m,4H), 9.6 (s,1H); ν($CHCl_3$) 3410, 3360 cm^{-1}; ν(Nujol) 1720, 1560, 1510 cm^{-1}.

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