1,11-Dipolar Cycloaddition

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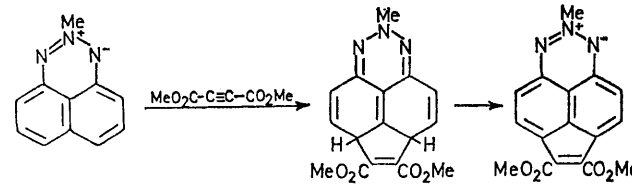
Summary 2-Methylnaphtho[1,8-*de*]triazine undergoes 1,11-dipolar ($12\pi + 2\pi$) cycloaddition to acetylenic esters to give 2-methylacenaphtho[5,6-*de*]triazines, after spontaneous dehydrogenation.

2-METHYLNAPHTHO[1,8-*de*]TRIAZINE (**1**)[1] is of interest since it incorporates the dipolar azimine function[2] for which the first 1,3-dipolar cycloaddition reactions have only recently been observed.[3]

Gradual addition of dimethyl acetylenedicarboxylate (2 equiv.) to the blue naphthotriazine (**1**) in refluxing *o*-dichlorobenzene over 3 h gave the red acenaphtho[5,6-*de*]-triazine (**3**) (30—40%), m.p. 233°. The ^{1}H n.m.r. spectrum of (**3**) [τ($CDCl_3$) 1·05 and 2·19 (4H, ABq, J 8·5 Hz), 5·08 (s, *N*-Me), and 5·88 (2 identical Me)] and its u.v. spectrum in ethanol [λ_{max} 247 (ϵ 18,500), 276 (13,200), 340sh (38,500), 352 (51,400), and 504 nm (6230)] are closely analogous to those reported for 2-methylacenaphtho[5,6-*de*]triazine.[4]

Formation of (**3**) is rationalised by a thermally allowed 1,11-dipolar cycloaddition to give (**2**), followed by dehydrogenation to give the stable 14π aromatic system. In accord with this, the reaction was cleaner and the best yield was obtained in the presence of 3 equiv. of sulphur as dehydrogenating agent.



(1) (2) (3)

Analogous cycloadditions were observed with diethyl acetylenedicarboxylate and methyl propiolate, but initial indications are that reactions with olefinic dipolarophiles are more complex. 2-(2,4-Dinitrophenyl)naphtho[1,8-*de*]-triazine reacts in a similar manner to the 2-methyl compound.

These reactions provide the first examples of $12\pi + 2\pi$ cycloaddition and, together with the recently reported 1,5-dipolar cycloaddition reactions,[5] strikingly illustrate the potential extension of 1,3-dipolar cycloaddition to vinylogous dipolar systems of more than 4π electrons.

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