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CYCLOADDITION OF IMIDAZO[2,1-b]THIAZOLES AND THIAZOLO[3,2-a]-BENZIMIDAZOLE WITH DIMETHYL ACETYLENEDICARBOXYLATE

Noritaka ABE, Tarozaemon NISHIWAKI, and Noriko KOMOTO
Department of Chemistry, Faculty of Sciences,
Yamaguchi University, Yamaguchi 753

Cycloadditions of imidazo[2,1-b]thiazole and thiazolo[3,2-a]-benzimidazole with dimethyl acetylenedicarboxylate follow dual courses producing pyrrolo[2,1-b]thiazoles in an aprotic nonpolar solvent or imidazo[1,2-a]pyridines in an aprotic polar solvent.

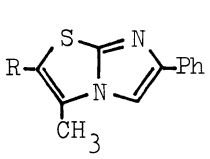
Cycloadditions of nitrogeneous heterocycles with acetylenic esters are receiving attention.[1] Our success in the reactions of azaazulenes with dimethyl acetylenedicarboxylate[2] prompted us to extend the study to aromatic azapentalenes,[3] among which only meso-ionic azapentalenes have been taken up as the substrate for cycloadditions with reactive acetylenes in the past.[4] We now report the reaction of imidazo[2,1-b]thiazoles which are one of the representative neutral aromatic azapentalenes.

When ethyl 3-methyl-6-phenylimidazo[2,1-b]thiazole-2-carboxylate (1a) was heated under reflux with dimethyl acetylenedicarboxylate (DMAD) in xylene for 27 h, 2-ethyl 6,7-dimethyl 3-methylpyrrolo[2,1-b]thiazole-2,6,7-tricarboxylate (2a)[5] [white needles (from EtOH), mp 167°C, ^{1}H NMR ($CDCl_3$) δ 1.34 (t, J=7 Hz, 3H), 2.75 (s, 3H), 3.90 (s, 6H), 4.37 (q, J=7 Hz, 2H), and 7.58 (s, 1H)] was isolated in 63% yield by silica gel chromatography. However, when the reaction was carried out in acetonitrile at room temperature for 11 days, tetramethyl 3-phenylimidazo[1,2-a]-pyridine-5,6,7,8-tetracarboxylate (3)[5] [yellow needles (from EtOH), mp 153°C, ^{1}H NMR ($CDCl_3$) δ 3.20, 3.90, 3.93, 4.10 (each s, 12H), 7.3-7.6 (m, 5H), and 7.85 (s, 1H)] was obtained in 40% yield together with 2a (13%).

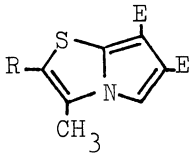
The reaction of 1b with DMAD proceeded similarly to give 2b[5] [50%, white needles (from EtOH), mp 149°C, ^{1}H NMR ($CDCl_3$) δ 2.43 (d, J=0.5 Hz, 3H), 3.90 (s, 6H), 6.62 (q, J=0.5 Hz, 1H), and 7.62 (s, 1H)] in hot xylene or 3 (23%) in acetonitrile at room temperature. To obtain more insight into the reaction course in the latter solvent, 3-methylthiazolo[3,2-a]benzimidazole (4) was allowed to react with DMAD in acetonitrile. The sulfur-containing moiety was again eliminated in this reaction, from which tetramethyl pyrido[1,2-a]benzimidazole-1,2,3,4-tetracarboxylate (5)[5] [yellow needles (from ligroin-benzene), mp 147°C, ^{1}H NMR ($CDCl_3$) δ 3.90, 3.92, 4.08 4.20 (each s, 12H), 7.3-7.8 (m, 3H), and 8.07 (dm, J=8 Hz, 1H)] was isolated in 24% yield.

These reactions may be rationalized in terms of the Diels-Alder addition in the aprotic non polar solvent and the 1,4-dipolar cycloaddition in the aprotic polar

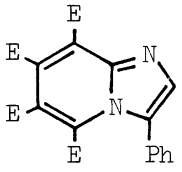
solvent as shown in the scheme. Italian workers previously studied the reaction of 1 with maleic anhydride and diethyl azodicarboxylate, but the only product they could isolate was the C-5-substituted one.[6]



1a: R=CO_2Et
1b: R=H



2a: R=CO_2Et
2b: R=H



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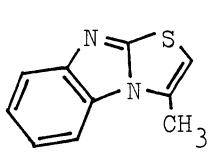

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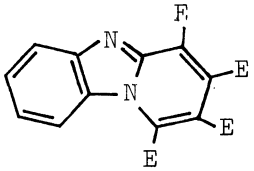

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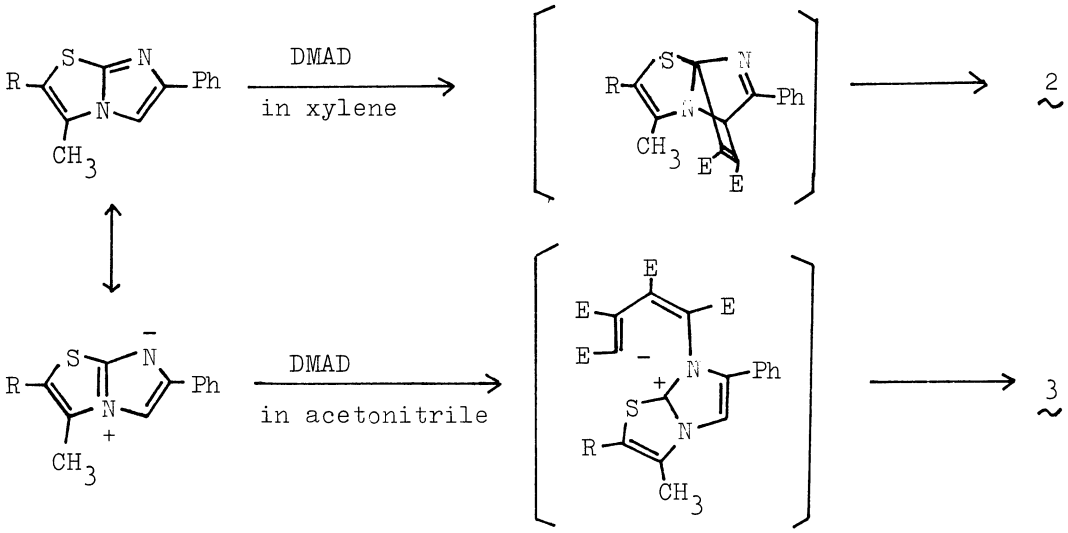
E=CO_2CH_3



References and Notes

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4) C. A. Ramsden, Tetrahedron, 33, 3203 (1977); K. Matsumoto and T. Uchida, Chem. Lett., 1978, 1093; K. T. Potts, S. K. Datta, and J. L. Marshall, J. Org. Chem., 44, 622 (1979); H. Gotthordt and F. Reiter, Chem. Ber., 112, 266 (1979).
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