

CYCLOADDITION OF THIAZOLO[3,2-a]BENZIMIDAZOLE AND IMIDAZO[2,1-b]BENZOTHIAZOLE WITH METHYL PROPIOLATE; FORMATION OF THIAZOLO[3,2-a][1,5]-BENZODIAZEPINE AND [1,4]DIAZEPINO[7,1-b]BENZOTHIAZOLE¹

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Abstract - 3-Methylthiazolo[3,2-a]benzimidazole and 2-methylimidazo[2,1-b]benzothiazole, respectively, react with methyl propiolate to give 1:2-adducts which are characterized as methyl (Z)-11-(methoxycarbonyl)-3-methyl-10-thiazolo[3,2-a][1,5]benzodiazepinacrylate and methyl (Z)-5-(methoxycarbonyl)-2-methyl-4-[1,4]diazepino[7,1-b]benzothiazolacrylate.

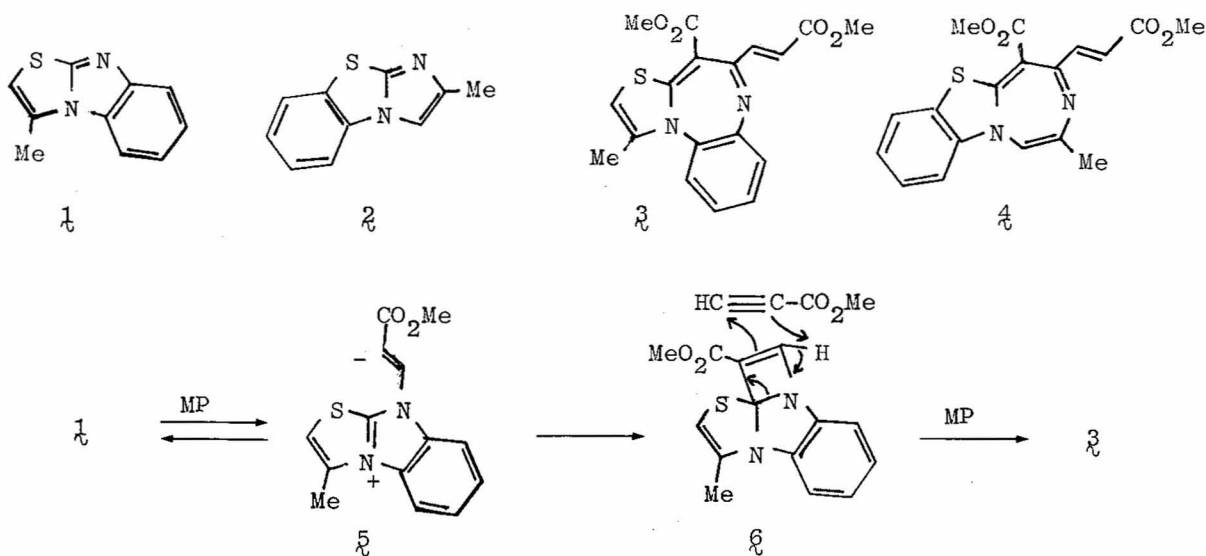
Cycloadditions of aromatic azapentalenes had received no attention² before we reported the reactions of imidazo[2,1-b]thiazoles, 3-methylthiazolo[3,2-a]benzimidazole (1), and 2-methylimidazo[2,1-b]benzothiazole (2) with dimethyl acetylenedicarboxylate (DMAD),³ which gave a product arising by loss of a nitrile from a 1:1-cycloadduct or a thiophene from a 1:2-cycloadduct. Our subsequent studies have revealed that the reactions of 1 or 2 with methyl propiolate (MP) follow a course completely different from that of DMAD and afford 1:2-adducts possessing novel heterocyclic ring systems.

When 1 was heated under reflux with an excess of MP in acetonitrile for 20 h, a 1:2-adduct⁴ was isolated in 39% yield and characterized as methyl (Z)-11-(methoxycarbonyl)-3-methyl-10-thiazolo[3,2-a][1,5]benzodiazepinacrylate (3) [orange needles (from benzene-cyclohexane), mp 185-186°C] from its spectral properties including mass [m/e 356 (M^+)], i.r. [ν_{\max} . (nujol) 1710 (C=O) and 960 cm^{-1} [(Z)-CH=CH]], and u.v. [λ_{\max} . (EtOH) 245 (log ϵ 4.37), 316 (4.19), 360 (4.14), and 430 nm (4.14)]. Its ¹H NMR spectrum (CDCl₃) showed AB doublets characteristic of (Z)-disposed vinyl protons at δ 6.07 and 7.75 (J 16 Hz). The proton at δ 5.72 to be assigned to the H-2 was long-range coupled with the C(3)-Me protons at δ 2.68 (J 0.5 Hz). Other signals are seen at δ 3.78 (3H, s, CO₂Me), 3.96 (3H, s, CO₂Me), and 7.15-7.9 (4H,

m, H-5,6,7,8).

Similarly, **2** gave methyl (Z)-5-(methoxycarbonyl)-2-methyl-4-[1,4]diazepino[7,1-b]-benzothiazolacrylate (**4**)⁴ in 81% yield after heating with an excess of MP in acetonitrile for 8 h [**4**: yellow prisms (from ethanol-benzene), mp 189–190°C, mass [m/e 356 (M⁺)], i.r. [ν_{max} (nujol) 1720 and 1700 (C=O) and 975 cm⁻¹ [(Z)-CH=CH]], u.v. [λ_{max} (CHCl₃) 261^{sh} (log ϵ 4.20), 295 (4.21), 320 (4.13), 337 (4.08), and 398 nm (4.45)], ¹H NMR [δ (CDCl₃) 2.28 (3H, bs, Me), 3.78 (3H, s, CO₂Me), 3.88 (3H, s, CO₂Me), 6.02 (1H, d, J 16 Hz, vinyl-H), 7.28 (1H, bs, H-1), 7.2–7.5 (4H, m, H-7,8, 9,10), 7.78 (1H, d, J 16 Hz, vinyl-H)]].

A plausible mechanism for the reaction of **1** with MP is shown in the Scheme. The reaction proceeds via a dipolar cycloaddition with MP to form intermediates, **5** and **6**, successively, and a further reaction of **6** with MP accompanied by a ring-enlargement would lead to the formation of **3**. The reactions of **1** and **2** with DMAD were found to proceed through a 1,4-dipolar cycloaddition.³ However, a reaction of the intermediate **5** with an additional molecule of MP is impossible owing to the lower reactivity of the latter⁵ and hence the intermediate **5** would be stabilized by an intramolecular cyclization.



References and Note

1. Part 3 of Studies on Heteropentalenes. Part 2, see Ref. 3.
2. J. Elguero, R. M. Claramunt, and A. J. H. Summers, *Adv. Heterocyclic Chem.*, 1978, **22**, 183.
3. N. Abe, T. Nishiwaki, and N. Komoto, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 3308.
4. Satisfactory elemental analyses were obtained for all new compounds.
5. J. I. Dickstein and S. I. Miller, *The Chemistry of the Carbon-carbon Triple Bond*, eds. by S. Patai, John Wiley & Sons, New York, 1978, chap. 19.

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