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]BENZOTHIAZOLE[1]

Noritaka Abe and Tarozaemon Nishiwaki
Department of Chemistry, Faculty of Sciences, Yamaguchi University, Yamaguchi 753, Japan

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.

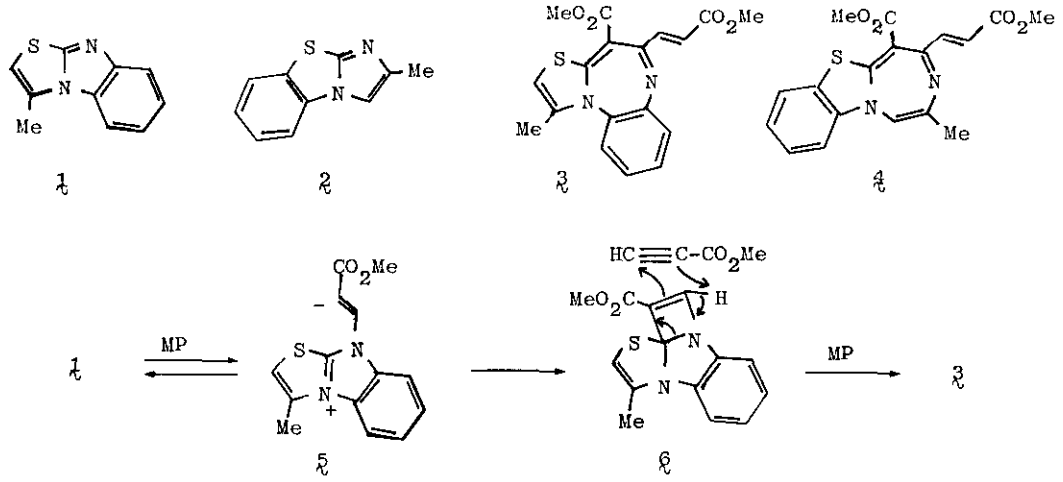
Cycloadditions of aromatic azapentalenes had received no attention[2] before we reported the reactions of imidazo[2,1-b]thiazoles, 3-methylthiazolo[3,2-a]benzimidazole (1), and 2-methylimidazo[2,1-b]benzothiazole (2) with dimethyl acetylenedicarboxylate (DMAD),[3] which gave a product arising by loss 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-adduct[4] 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. [$\nu_{max.}$ (nujol) 1710 (C=O) and 960 cm^{-1} [(Z)-CH=CH]], and u.v. [$\lambda_{max.}$ (EtOH) 245 (log ε 4.37), 316 (4.19), 360 (4.14), and 430 nm (4.14)]. Its ^1H NMR spectrum ($CDCl_3$) 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, CO_2Me), 3.96 (3H, s, CO_2Me), 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. [$\nu_{max.}$ (nujol) 1720 and 1700 (C=O) and 975 cm^{-1} [(Z)-CH=CH)], u.v. [$\lambda_{max.}$ ($CHCl_3$) 261^{sh} (log ε 4.20), 295 (4.21), 320 (4.13), 337 (4.08), and 398 nm (4.45)], ^{1}H NMR [δ ($CDCl_3$) 2.28 (3H, bs, Me), 3.78 (3H, s, CO_2Me), 3.88 (3H, s, CO_2Me), 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 latter[5] 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.

Received, 9th December, 1980