Cycloaddition of Thiazolo[3,2-a]benzimidazole and Imidazo[2,1-b]benzo-
thiazole with Methyl Propiolate; Formation of Thiazolo[3,2-a][1,5]-
benzodiazepine and [1,4]Diazepino[7,1-b]benzothiazole

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Abstract — 3-Methylthiazolo[3,2-a]benzimidazole and 2-methyl-
imidazo[2,1-b]benzothiazole, respectively, react with methyl
propiolate to give 1:2-adducts which are characterized as methyl
(3)-11-(methoxycarbonyl)-3-methyl-10-thiazolo[3,2-a][1,5]benzo-
diazepinacrylate and methyl (3)-5-(methoxycarbonyl)-2-methyl-4-

Cycloadditions of aromatic azapentalenes had received no attention before we
reported the reactions of imidazo[2,1-b]thiazoles, 3-methylthiazolo[3,2-a]benz-
imidazole (1), and 2-methylimidazo[2,1-b]benzothiazole (2) with dimethyl acetylene-
dicarboxylate (DMAD), 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 was isolated in 39% yield and characterized as methyl (3)-11-(methoxycarbon-
yl)-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. [νmax. (nujol) 1710 (C=O) and 960 cm⁻¹ [{(3)-CH=CH}], and u.v.
[λmax. (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 (3)-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, $^2_2$ gave methyl (Z)-5-(methoxycarbonyl)-2-methyl-4-[1,4]diazepino[7,1-b]-benzothiazolacrylate ($^4_3$) in 81% yield after heating with an excess of MP in acetonitrile for 8 h ($^4_3$: yellow prisms from ethanol-benzene), mp 189-190° C, mass [m/e 356 (M$^+$)], i.r. [$\nu_{\text{max}}$ (nujol) 1720 and 1700 (C=O) and 975 cm$^{-1}$ ([Z]-CH=CH)], u.v. [$\lambda_{\text{max}}$ (CHCl$_3$) 261$^\text{sh}$ (log $\varepsilon$ 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$_2$Me), 3.88 (3H, s, CO$_2$Me), 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 $^1_1$ with MP is shown in the Scheme. The reaction proceeds via a dipolar cycloaddition with MP to form intermediates, $^5_5$ and $^6_6$, successively, and a further reaction of $^6_6$ with MP accompanied by a ring-enlargement would lead to the formation of $^3_3$. The reactions of $^1_1$ and $^2_2$ with DMAD were found to proceed through a 1,4-dipolar cycloaddition. However, a reaction of the intermediate $^5_5$ with an additional molecule of MP is impossible owing to the lower reactivity of the latter and hence the intermediate $^5_5$ would be stabilized by an intramolecular cyclization.

References and Note
1. Part 3 of Studies on Heteropentalenes. Part 2, see Ref. 3.
4. Satisfactory elemental analyses were obtained for all new compounds.

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