Communications to the Editor

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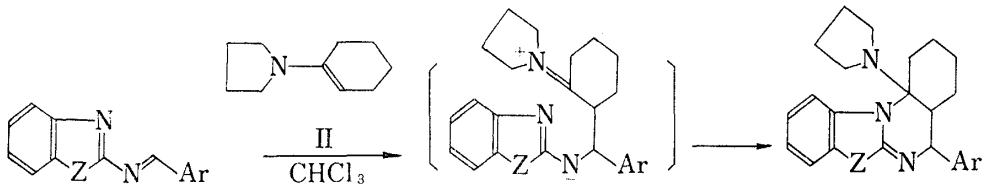
1,4-Cycloaddition Reactions of Enamine with Compounds containing the Double Bond System C=N–C=N

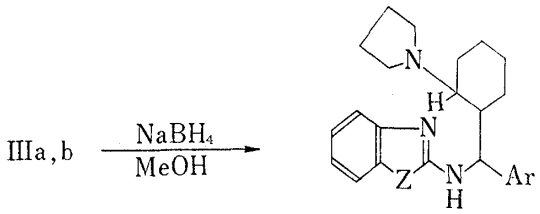
1-(1-Pyrrolidinyl)cyclohexene reacts with 2-(*p*-nitrobenzylideneamino)benzoxazole and 2-(*p*-nitrobenzylideneamino)benzimidazole, affording new Diels–Alder type adducts respectively.

While the cycloaddition reactions of enamines to the conjugated C=C groups have been extensively investigated, their reactions with conjugated C=N groups have received little attention.[1] Cycloadditions of enamine with benzofurazan,[2] 4,6-diphenyl-1,2,3,5-oxathiadiazine-2,2-dioxide,[3] and heterocumulene[4] have been reported. In this paper, we wish to report a 1,4-cycloaddition of enamine with 2-(*p*-nitrobenzylideneamino)benzoxazole (Ia) and with 2-(*p*-nitrobenzylideneamino)benzimidazole (Ib).

Refluxing of a solution of Ia [mp 288—289°] and 1-(1-pyrrolidinyl)cyclohexene (II) in chloroform for 30 min gave the Diels–Alder type adduct IIIa [mp 160—162° (decomp.)] in 37% yield. *Anal.* Calcd. for $C_{24}H_{26}O_3N_4$: C, 68.88; H, 6.26; N, 13.39. Found: C, 68.61; H, 6.12; N, 13.22. IR ν_{max}^{KBr} cm^{-1}: 1697 (C=N). NMR ($CDCl_3$) δ: 0.90—3.10 (17H, m, methine and methylene protons), 5.40 (1H, d, J=4.0 Hz, =N–C<u>H</u>–), 6.91—7.15 (4H, m, C-6,7,8,9-protons), 7.57 (2H, d, J=8.0 Hz, C-2′,6′-protons), 8.12 (2H, d, J=8.0 Hz, C-3′,5′-protons). Mass Spectrum *m/e*: 418 (M^+).



Ia,b IIIa,b



IVa,b

a : Z=O, Ar=*p*-NO_2–C_6H_4
b : Z=NH, Ar=*p*-NO_2–C_6H_4

Chart 1

1) For a review, see: A.G. Cook, "Enamines," Marcel Dekker, New York and London, 1969. p.
2) L. Marchetti and G. Tosi, *Ann. Chem.* (Rome), **57**, 1414 (1967) [*C. A.*, **69**, 2934*f* (1968)]; M.J. Haddadin and C.H. Issidorides, *Tetrahedron Letters.*, **1965**, 3253; J.W. McFarland, *J. Org. Chem.*, **36**, 1842 (1971); N.A. Mufarrij, M.J. Haddadin, C.H. Issidorides, J.W. McFarland, and J.D. Johnston, *J. Chem. Soc. Perkin I*, **1972**, 965; M. Sakamoto, M. Shibano, and Y. Tomimatsu, *Yakugaku Zasshi*, **93**, 1643 (1973).
3) H. Weidinger and H.J. Sturm, *Ann. Chem.*, **716**, 143 (1968).
4) S. Hünig and K. Hübner, *Chem. Ber.*, **95**, 937 (1962); J. Goerdeler and H. Schenk, *ibid.*, **98**, 3831 (1965); R.W.J. Carney, J. Wojtkunski, and G. deStevens, *J. Org. Chem.*, **29**, 2887 (1964); H.M. Blatter and H. Lukaszewski, *ibid.*, **31**, 722 (1966); G. deStevens, B. Smolinsky, and L. Dorfman, *ibid.*, **29**, 1115 (1964).

Hydrogenolysis of IIIa with $NaBH_4$ in methanol gave the corresponding compound, IVa [mp 93—95° (decomp.), $C_{24}H_{28}O_3N_4$ (Mass Spectrum *m/e*: 420 (M^+)]. In the infrared (IR) spectrum of IVa, the absorption (1697 cm^{-1}) due to the stretching band of imine (C=N) in IIIa disappeared and a sharp absorption appeared at 3197 cm^{-1} due to the secondary amino group. Furthermore, its nuclear magnetic resonance (NMR) spectrum (in d_6-DMSO) indicated signals at δ 1.08—2.64 (18H, m, methine and methylene protons), 5.21 (1H, t, J=10.0 Hz, –NH–CH–), 6.90—7.36 (4H, m, C-4,5,6,7-protons), 7.70 (2H, d, J=8.0 Hz, C-2′,6′-protons), 8.11 (2H, d, J=8.0 Hz, C-3′,5′-protons), 8.57 (1H, d, J=10.0 Hz, –NH–CH–). The signal at δ 8.57 disappeared on addition of D_2O.

Similarly, IIIb [mp 229—230° (decomp.)] was obtained from Ib [mp 264—267° (decomp.)] and II in 32% yield. *Anal.* Calcd. for $C_{24}H_{27}O_2N_5$: C, 69.04; H, 6.52; N, 16.78. Found: C, 68.93; H, 6.58; N, 16.81. IR ν_{max}^{KBr} cm^{-1}: 1642 (C=N). NMR ($CDCl_3$) δ: 1.14—2.90 (17H, m, methine and methylene protons), 4.81 (1H, d, J=3.0 Hz, =N–CH–), 6.28—7.21 (4H, m, C-6,7,8,9-protons), 7.69 (2H, d, J=8.0 Hz, C-2′,6′-protons), 8.10 (2H, d, J=8.0 Hz, C-3′,5′-protons), 9.74 (1H, broad, –NH–). Mass Spectrum *m/e*: 417 (M^+). Hydrogenolysis of IIIb with $NaBH_4$ in methanol gave the corresponding compound IVb [mp 278—279° (decomp.), $C_{24}H_{29}O_2N_5$ (Mass Spectrum *m/e*: 419 (M^+)].

The similar reaction of II with 2-(*p*-anisylideneamino)benzoxazole and 2-(*p*-anisylideneamino)benzimidazole respectively resulted in the recovery of starting material quantitatively.

The preceding observations indicate that the presence of electron releasing group at 4′-position inhibits the cycloaddition reaction of I with II presumably by increasing electron density at carbon atom of C=N group.

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