

## 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.<sup>1)</sup> Cycloadditions of enamine with benzofurazan,<sup>2)</sup> 4,6-diphenyl-1,2,3,5-oxathiadiazine-2,2-dioxide,<sup>3)</sup> and heterocumulene<sup>4)</sup> 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<sub>24</sub>H<sub>26</sub>O<sub>3</sub>N<sub>4</sub>: C, 68.88; H, 6.26; N, 13.39. Found: C, 68.61; H, 6.12; N, 13.22. IR  $\nu_{\max}^{\text{KBr}}$  cm<sup>-1</sup>: 1697 (C=N). NMR (CDCl<sub>3</sub>)  $\delta$ : 0.90–3.10 (17H, m, methine and methylene protons), 5.40 (1H, d, *J*=4.0 Hz, =N-CH-), 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<sup>+</sup>).

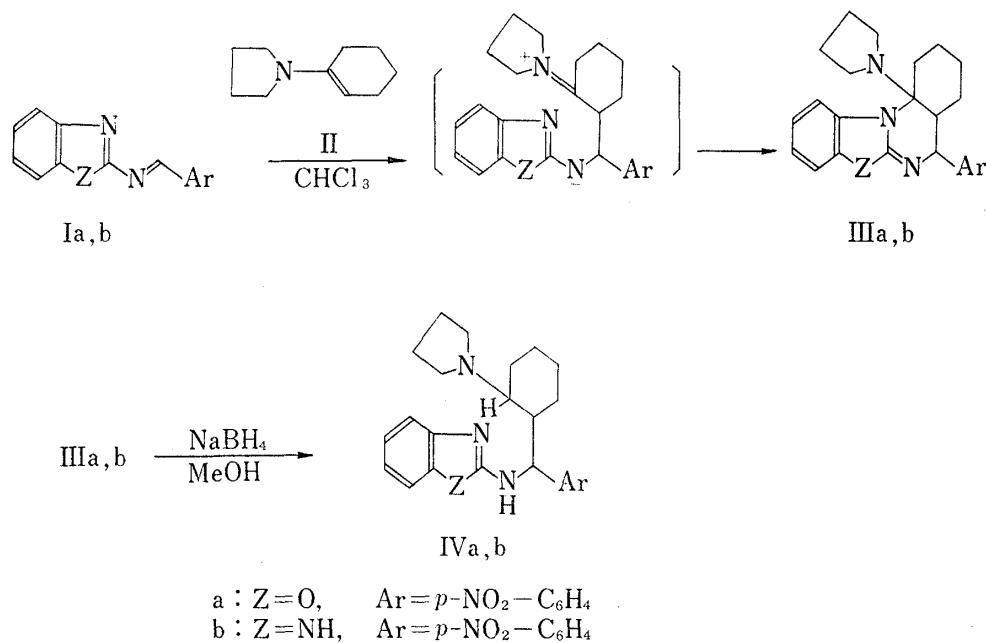


Chart 1

- 1) For a review, see: A.G. Cook, "Enamines," Marcel Dekker, New York and London, 1969. p.
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- 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  $\text{NaBH}_4$  in methanol gave the corresponding compound, IVa [mp 93—95° (decomp.),  $\text{C}_{24}\text{H}_{28}\text{O}_3\text{N}_4$  (Mass Spectrum  $m/e$ : 420 ( $\text{M}^+$ )). In the infrared (IR) spectrum of IVa, the absorption ( $1697\text{ cm}^{-1}$ ) due to the stretching band of imine ( $\text{C}=\text{N}$ ) in IIIa disappeared and a sharp absorption appeared at  $3197\text{ cm}^{-1}$  due to the secondary amino group. Furthermore, its nuclear magnetic resonance (NMR) spectrum (in  $d_6$ -DMSO) indicated signals at  $\delta$  1.08—2.64 (18H, m, methine and methylene protons), 5.21 (1H, t,  $J=10.0\text{ Hz}$ ,  $-\text{NH}-\dot{\text{C}}\text{H}-$ ), 6.90—7.36 (4H, m, C-4,5,6,7-protons), 7.70 (2H, d,  $J=8.0\text{ Hz}$ , C-2',6'-protons), 8.11 (2H, d,  $J=8.0\text{ Hz}$ , C-3',5'-protons), 8.57 (1H, d,  $J=10.0\text{ Hz}$ ,  $-\text{NH}-\dot{\text{C}}\text{H}-$ ). The signal at  $\delta$  8.57 disappeared on addition of  $\text{D}_2\text{O}$ .

Similarly, IIIb [mp 229—230° (decomp.)] was obtained from Ib [mp 264—267° (decomp.)] and II in 32% yield. *Anal.* Calcd. for  $\text{C}_{24}\text{H}_{27}\text{O}_2\text{N}_5$ : C, 69.04; H, 6.52; N, 16.78. Found: C, 68.93; H, 6.58; N, 16.81. IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 1642 ( $\text{C}=\text{N}$ ). NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.14—2.90 (17H, m, methine and methylene protons), 4.81 (1H, d,  $J=3.0\text{ Hz}$ ,  $=\text{N}-\dot{\text{C}}\text{H}-$ ), 6.28—7.21 (4H, m, C-6,7,8,9-protons), 7.69 (2H, d,  $J=8.0\text{ Hz}$ , C-2',6'-protons), 8.10 (2H, d,  $J=8.0\text{ Hz}$ , C-3',5'-protons), 9.74 (1H, broad,  $-\text{NH}-$ ). Mass Spectrum  $m/e$ : 417 ( $\text{M}^+$ ). Hydrogenolysis of IIIb with  $\text{NaBH}_4$  in methanol gave the corresponding compound IVb [mp 278—279° (decomp.),  $\text{C}_{24}\text{H}_{29}\text{O}_2\text{N}_5$  (Mass Spectrum  $m/e$ : 419 ( $\text{M}^+$ )).

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  $\text{C}=\text{N}$  group.

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