Studies on Heteroaromaticity. XXV.[1] 1,3-Dipolar Cycloaddition of *C*-(2-Benzimidazolyl)-*N*-phenylnitrone

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In continuation from the previous papers concerning the heterocyclic nitrones involving nitrofuran-[1] and pyrimidine-ring,[2] this paper deals with a nitrone having a benzimidazole ring and its 1,3-dipolar cycloaddition reactivity with dipolarophilic olefins such as styrene and methyl acrylate. *C*-(2-Benzimidazolyl)-*N*-phenylnitrone (I) was readily prepared from benzimidazole-2-carboxaldehyde[3] and phenylhydroxylamine in a 55% yield by the routine procedure.[4] I was relatively stable and could be stored in a brown desiccator but readily decomposed to colored tars in the light.

As typical examples of its 1,3-dipolar cycloaddition reactions, styrene and methyl acrylate were treated in dioxane with I affording the corresponding adducts, II and III, in 40 and 50% yields, respectively. Each structure of both compounds, II and III, was determined by the NMR spectrum. Figure 1 shows the NMR spectrum of III as an example. The existence of two quartets around 4.55 and 5.01 τ for two methine protons of an isoxazolidine ring in the NMR spectrum supports structure III, which is 5- instead of 4-carbomethoxy structure.[1] Similarly, II is concluded to have 5-phenylisoxazolidine ring. Such a constant direction of the addtion irrespective of the electronic character of a substituent of the olefin demonstrates that this reaction proceeds in the manner similar to that in the case of *C*-(5-nitro-2-furyl)-*N*-phenylnitrone,[1] both followed by the general principle suggested by Huisgen.[5]

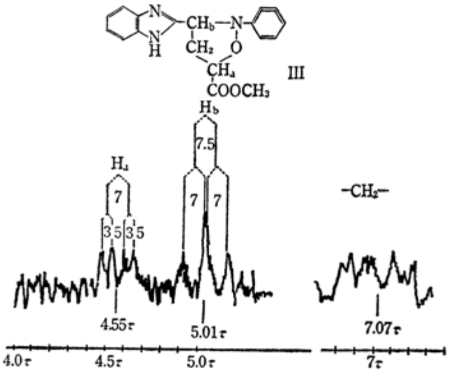

Fig. 1. NMR spectrum of III (DMSO-d_6).

Experimental[6]

Preparation of *C*-(2-Benzimidazolyl)-*N*-phenylnitrone (I). A solution of 6 g (41 mmol) of benzimidazole-2-carboxaldehyde[3] and 8 g (40 mmol) of phenylhydroxylamine[7] in 400 m*l* of ethanol was refluxed for two days. The precipitates were collected after cooling, washed with acetone and recrystallized from ethanol to give 5.3 g (55%) of I as yellow needles, mp 245—248°C (decomp). IR (KBr) cm^{-1}: 1565, 1580 ($\nu_{C=N}$), 1065 ($\nu_{N\rightarrow O}$). UV λ_{max}^{EtOH} mμ (log ε): 355 (4.45).

Found: C, 71.21; H, 4.56; N, 17.90%. Calcd for $C_{14}H_{11}ON_3$: C, 70.87; H, 4.67; N, 17.71%.

Reaction of I with Styrene. A solution of 0.3 g (1.3 mmol) of I and 0.2 g (1.9 mmol) of styrene in 30 m*l* of dioxane was heated at 90°C on a water bath for 27 hr. After dioxane was removed under reduced pressure, the residual oil was dissolved in a small amount of chloroform and made turbid by addition of petroleum ether. A separated oil solidified gradually in an ice box. The separated crystals were collected and recrystallized from chloroform-ether to give 0.11 g (40%) of II as colorless powders, mp 178—180°C. In the infrared spectrum, a $\nu_{N\rightarrow O}$ absorption disappeared and a new one appeared at 1620 cm^{-1} due to $\nu_{C=N}$. UV λ_{max}^{EtOH} mμ (log ε): 238 (4.27), 274 (4.01), 280 (4.02).

Found: C, 77.35; H, 5.38; N, 11.84%. Calcd for $C_{22}H_{19}ON_3$: C, 77.39; H, 5.61; N, 12.31%.

Reaction of I with Methyl Acrylate. A solution of 0.3 g (1.3 mmol) of I and 0.2 g (2.3 mmol) of methyl acrylate in 26 m*l* of dioxane was heated at 90°C on a water bath for 25 hr. Work-up as above afforded 0.17 g (50%) of III as colorless crystals, mp 172—174°C. IR (KBr) cm^{-1}: 1740 (ν_{CO}), 1620 ($\nu_{C=N}$), UV λ_{max}^{EtOH} mμ (log ε): 238 (3.60), 275 (3.57), 280 (2.57).

Found: C, 66.71; H, 5.08; N, 12.73%. Calcd for $C_{18}H_{17}O_3N_3$: C, 66.86; H, 5.30; N, 13.00%.

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[1] Part XXIV of this series: T. Sasaki, T. Yoshioka and I. Izure, This Bulletin, **41**, 2964 (1968).

[2] As Part XXI of this series: T. Sasaki and M. Ando, This Bulletin, **41**, 2960 (1968).

[3] H. R. Hensel, *Chem. Ber.*, **98**, 1325 (1965).

[4] L. I. Smith, *Chem. Revs.*, **23**, 193 (1938).

[5] R. Huisgen, L. Feiler and G. Binsch, Angew. *Chem. Intern. E. Engl.*, **3**, 753 (1964); J. C. Martin, V. W. Goodlett and R. D. Burpitt, *J. Org. Chem.*, **30**, 4309 (1965).

[6] All the melting points were not corrected. Infrared spectra were determined on a Nippon-Bunko, Model IR-S spectrometer and electronic spectra were obtained with a Nippon-Bunko optical rotatry dispersion recorder, Model ORD/UV-5. NMR spectra were determined on a Varian A-60 spectrometer, with tetramethylsilane as an internal standard and the peak positions are expressed by τ-values.

[7] O. Kamm, "Org. Synth.," Coll. Vol. 1, p. 445 (1956).