

Synthesis and Reactivities of 1-Carbobenzoxy-3-substituted-aziridinones

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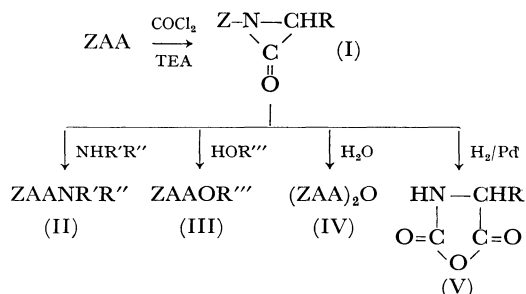
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Interest in aziridinones has increased since Baumgarten¹⁾ first proved the existence of *N*-*t*-butyl-3-phenylaziridinone by spectral studies. Recently, some analogues were obtained in crystalline forms and their chemical properties were reported.²⁻⁶⁾

I wish to report a new synthetic route and the reactivities of 1-carobenzoxy-3-substituted-aziridinones (I) derived from the corresponding carbobenzoxy-L-amino acids (ZAA). Dehydration of ZAA was carried out successfully in THF at -20°C , with the aid of dehydrating agents containing two reactive halogen atoms in the molecule (COCl_2 , SOCl_2 , POCl_3 , etc.), and subsequently by dropwise addition of triethylamine (TEA) exactly to neutralize. 1-carobenzoxy-3-benzylaziridinone (Ia) was obtained as crystalline needles, mp 73.0°C —

73.5°C . $[\alpha]_{\text{D}}^{20} -36.0^{\circ}$ ($c=1$, THF), mass M^{+} 281. NMR (CDCl_3 , δ): 7.21 (*bs*, 5H), 7.37 (*bs*, 5H), 5.30 (*s*, 2H), 4.55 (*t*, 1H), 3.26 (*dd*, 2H), 3.03 (*dd*, 2H). Found: C, 72.60; H, 5.33; N, 5.11%. Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_3$: C, 72.58; H, 5.37; N, 4.98%. I showed 1840 cm^{-1} band in IR (Fig. 1) which was characteristic of aziridinones.^{1,2)}

I was found to be quite sensitive to the nucleophiles and ring opening took place always between N and C=O bond selectively. Typical reactions with I are as follows.



Usually it was convenient for I to be treated directly with the desired nucleophile at -20°C without isolation from the reaction mixture. So far, no racemization has been observed (Table 1).

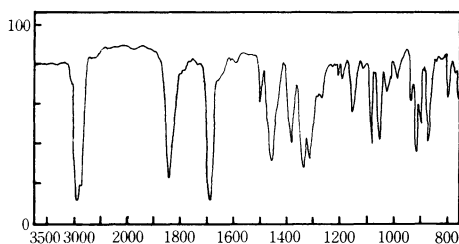


Fig. 1. IR spectrum of Ia.

TABLE 1. RESULTS OF REACTIONS WITH I

R	Nucleophile	Product	Yield (%)	mp ($^{\circ}\text{C}$)	$[\alpha]_{\text{D}}^{20}$ ($c=1$)
$\text{CH}_2\text{C}_6\text{H}_5$	$\text{H}\cdot\text{Gly}\cdot\text{OEt}$	(II)	83.8	111	-16.8 (EtOH)
$\text{CH}_2\text{C}_6\text{H}_5$	$\text{NHCHCO}_2\text{CH}_3$	(II)	81.0	81	-70.0 (MeOH)
	$\begin{array}{c} \text{H}_3\text{C} \\ \\ \text{CH}(\text{CH}_3)_2 \end{array}$				
$\text{CH}_2\text{C}_6\text{H}_5$	<i>t</i> -BuOH	(III)	83.3	82	-6.0 (EtOH)
$\text{CH}_2\text{C}_6\text{H}_5$	H_2O	(IV)	47.2	146	$+14.6$ (Dioxan)
$\text{CH}(\text{CH}_3)_2$	$\text{H}\cdot\text{Gly}\cdot\text{OEt}$	(II)	81.7	164	-27.0 (EtOH)
$\text{CH}(\text{CH}_3)_2$	MeOH	(III)	81.9	56	-18.9 (MeOH)
$\text{CH}(\text{CH}_3)_2$	H_2O	(IV)	45.6	98	$+10.7$ (THF)
CH_3	$\text{H}\cdot\text{Gly}\cdot\text{OEt}$	(II)	71.1	101	-22.2 (EtOH)
CH_3	H_2O	(IV)	45.2	122	-11.0 (THF)
$\text{CH}_2\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5$	$\text{H}\cdot\text{Phe}\cdot\text{OMe}$	(II)	72.4	116	-14.8 (DMF)

1) H. E. Baumgarten, R. L. Zey and U. Krolls, *J. Amer. Chem. Soc.*, **83**, 4469 (1961); H. E. Baumgarten, *ibid.*, **84**, 4975 (1962); H. E. Baumgarten and J. F. Fuerholzer, *ibid.*, **85**, 3303 (1963).

2) J. C. Sheehan and I. Lengyel, *ibid.*, **86**, 1356 (1964); J. C. Sheehan and J. H. Beeson, *ibid.*, **89**, 362 (1967); J. C. Sheehan and M. M. Nafissi-V, *ibid.*, **91**, 1176 (1969).

3) I. Lengyel and D. B. Uliss, *Chem. Commun.*, **1968**, 1621.

4) K. Bott, *Tetrahedron Lett.*, **1968**, 3323.

5) E. R. Talaty and A. E. Dupuy, Jr., *Chem. Commun.*, **1968**, 790; E. R. Talaty and C. M. Utermohlen, *ibid.*, **1970**, 473.

6) J. C. Sheehan and I. Lengyel, *Angew. Chem.*, **80**, 27 (1968).