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

Muneji Miyoshi

Chemical Research Laboratory, Tanabe Seiyaku Co., Ltd., Higashiyodogawa-ku, Osaka

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Interest in aziridinones has increased since Baumgarten[1] first proved the existence of *N*-*t*-butyl-3-phenylaziridinone by spectral studies. Recently, some analoges 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-carbobenzoxy-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-carbobenzoxy-3-benzylaziridinone (Ia) was obtained as crystalline needles, mp 73.0—73.5°C. $[\alpha]_D^{20}$ −36.0° ($c=1$, 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 $C_{17}H_{15}NO_3$: 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]

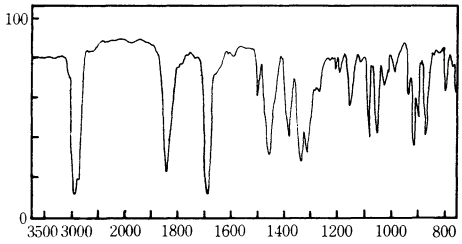
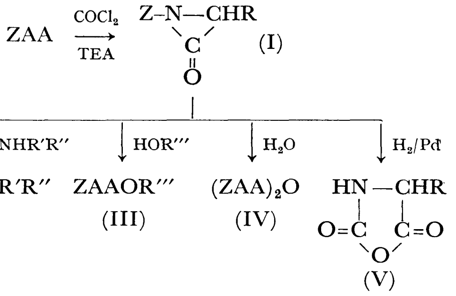


Fig. 1. IR spectrum of Ia.

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).

Table 1. Results of reactions with I

R	Nucleophile	Product	Yield (%)	mp (°C)	$[\alpha]_D^{20}$ ($c=1$)
$CH_2C_6H_5$	H·Gly·OEt	(II)	83.8	111	−16.8 (EtOH)
$CH_2C_6H_5$	$\underset{H_3C}{N}H\underset{CH(CH_3)_2}{C}HCO_2CH_3$	(II)	81.0	81	−70.0 (MeOH)
$CH_2C_6H_5$	*t*-BuOH	(III)	83.3	82	− 6.0 (EtOH)
$CH_2C_6H_5$	H_2O	(IV)	47.2	146	+14.6 (Dioxan)
$CH(CH_3)_2$	H·Gly·OEt	(II)	81.7	164	−27.0 (EtOH)
$CH(CH_3)_2$	MeOH	(III)	81.9	56	−18.9 (MeOH)
$CH(CH_3)_2$	H_2O	(IV)	45.6	98	+10.7 (THF)
CH_3	H·Gly·OEt	(II)	71.1	101	−22.2 (EtOH)
CH_3	H_2O	(IV)	45.2	122	−11.0 (THF)
$CH_2CO_2CH_2C_6H_5$	H·Phe·OMe	(II)	72.4	116	−14.8 (DMF)

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