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AZIRIDINONES. CYCLOADDITION REACTION OF AZIRIDINONE WITH PHENYL ISOCYANATE

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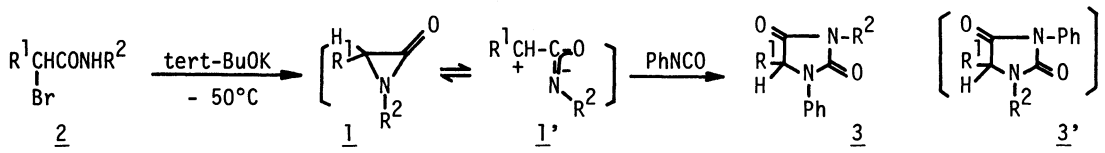
Aziridinone reacted with phenyl isocyanate to give two isomers of imidazolidine-2,4-dione which correspond to the cycloadducts of aziridinone to phenyl isocyanate.

In the ring opening reactions of three-membered cycles such as aziridine[2)] and cyclopropanone[3)], the three-membered ring is predominantly cleaved at the bond faced to the nitrogen atom in aziridine or the carbon atom of carbonyl group in cyclopropanone. These results indicate that the existence of nonbonding or pai electron on a three-membered ring may contribute to weaken the linkage faced to these centers. From this idea, the authors planned to investigate a behavior of aziridinone which contains both nitrogen atom and carbonyl group in the ring during its cycloaddition reaction. No cycloaddition reaction of aziridinone, however, has been reported to date.

Treatment of α-bromo-N-(p-tolyl)acetamide 2a with potassium tert-butoxide in dry tetrahydrofuran at -50°C for 1 hr and the ensuing addition of phenyl isocyanate gave a colorless product in 62% yield. This compound is a 1:1 adduct of phenyl isocyanate to aziridinone 1a and its IR spectrum showed the carbonyl stretching at 1770 and 1700 cm^{-1}. Although 1-phenyl-3-(p-tolyl)- (3a) and 3-phenyl-1-(p-tolyl)imidazolidine-2,4-dione (3a') are possible for the product, it was identical to the authentic 3a which was prepared by the other route as showen in scheme 1.



Scheme 1

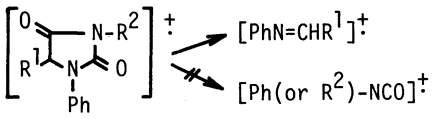
Sarel and Greenberger[4)] have reported α-chloro-N-phenylacetamide on the treatment with sodium amide had yielded piperazinedione and α-anilino-N-phenylacetamide which could be rationalized only via aziridinone intermediate. It is clear that aziridinones 1 have served as reactive species in our reactions, since 2 gave piperazinediones in the absence of phenyl isocyanate.

The results of the similar reactions from other α-bromoamides 2b-2f are summarized in table 1. The orientation of the cycloadducts 3 was confirmed on the basis of the fragmentation in mass spectra in which the first fragment ion peak from the parent

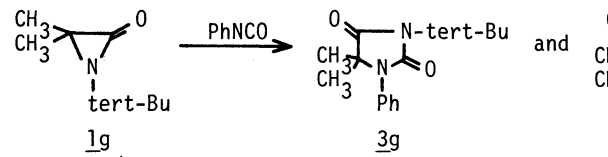
Table 1. The Reactions of 2 with Phenyl Isocyanate in the Presence of Potassium tert-Butoxide.

	R^1	R^2	Yield(%)	mp(°C)	$\nu_{CO}(cm^{-1})$	NMR in $CDCl_3$; τ
3a	H	p-CH_3-C_6H_4	62	152-154	1770, 1710	7.71(s, CH_3), 5.84(s, CH_2)
3b	H	p-Cl-C_6H_4	78	135-137	1770, 1710	7.60(s, CH_2)
3c	H	tert-Butyl	42	114-116	1760, 1700	8.32(s, $C(CH_3)_3$), 5.84(s, CH_2)
3d	CH_3	p-CH_3-C_6H_4	14	113-114	1770, 1710	8.52(d, CH_3CH), 7.68(s, CH_3), 5.36(q, CH_3CH)
3e	Ph	p-CH_3-C_6H_4	12	127-129	1770, 1710	7.71(s, CH_3), 4.72(s, CH)
3f	Ph	CH_3CH_2	37	132-133	1760, 1700	8.70(t, CH_3CH_2), 6.25(q, CH_3CH_2), 4.50(s, CH)

appeared at a molecular weight calculated for $PhN=CHR^1$ and no peak assignable to [Ph (or R^2)-NCO]$^{+\cdot}$ was observed. Furthermore, the spectroscopic investigation of the crude products showed that crude 3 might be contaminated with another cycloadducts 3′ which could not be isolated in a pure form. Thus, the mass spectra of pure 3a and 3b revealed each peak at m/e 105([$PhN=CH_2$]$^+$) as a base peak and no peak assignable to [CH_3(or Cl)-C_6H_4-NCO]$^+$ or [CH_3(or Cl)-$C_6H_4N=CH_2$]$^+$, but those of crude 3a and 3b showed the additional peaks at 119([CH_3-$C_6H_4N=CH_2$]$^+$) and 139, 141([Cl-$C_6H_4N=CH_2$]$^+$), respectively.



As mentioned above, most of aziridinones can exist as reacting intermediates in solution only at low temperature, while some aziridinones having bulky substituents such as tert-butyl or adamantyl group have been isolated even at room temperature. Then the reaction of stable 1-tert-butyl-3,3-dimethylaziridinone 1g with phenyl isocyanate was carried out and a mixture of two cycloadducts was obtained in 25% yield. Each isomers 3g and 3g′ were separated in a pure form by column chromatography on alumina(3g/3g′ = 7/3). 3g: mp 90-91°C; IR 1760, 1700 cm^{-1}(ν_{CO}); NMR(in $CDCl_3$) τ 8.62(s, CH_3), 8.33(s, $C(CH_3)_3$); Mass(m/e) 260(M^+), 204($M^+-C_4H_8$), 189(204^+-CH_3), 134($(CH_3)_2C{=}\overset{+}{N}HPh$), 118($CH_3C{\equiv}\overset{+}{N}Ph$). 3g′: mp 126.5-128°C; IR 1760, 1700 cm^{-1}(ν_{CO}); NMR(in $CDCl_3$) τ8.53(s, CH_3), 8.25(s, $C(CH_3)_3$); Mass(m/e) 260(M^+), 204($M^+-C_4H_8$), 119([PhNCO]$^+$).



Liebmann and Greengerg[5] have discussed about the stability of aziridinone and suggested that unstable aziridinones might exist in the open dipolar form 1′ rather than the cyclic form 1. If so, the formation of the cycloadducts 3 in our reactions would be the result from the combination of 1′ with phenyl isocyanate. On the other hand, the reaction with stable 1g would proceed partly via 1g′ to give 3g but the formation mechanism for 3g′ has not been clarified yet.

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