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CYCLOADDITIONS OF DIAZIRIDINONE

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Di-tert-butyldiaziridinone underwent cycloadditions to diphenylketene and benzoyl isocyanate, and to benzonitrile in the presence of Lewis acid as a catalyst.

We have found that three-membered heterocycles containing two heteroatoms, e.g. 2-alkyloxaziridines[1] or 1,2-dialkyldiaziridines,[2] gave 1:1 cycloadducts with isocyanates. In the case with diphenylketene, on the contrary, quite different products were obtained without any 1:1 cycloadduct.[1,3] It is interesting to see if the cycloaddition will be observed for a highly strained diaziridinone. Greene and his coworkers tried the cycloadditions of 1,2-di-tert-butyldiaziridinone to tetracyanoethylene and maleic anhydride, and reported that the cycloaddition to an unsaturated group was very difficult because of the steric hindrance of the tert-butyl group of diaziridinone.[4] We now wish to present the cycloadditions to a ketene, an isocyanate, and a nitrile.

The reaction between di-tert-butyldiaziridinone (1) and diphenylketene gives two isomers of the 1:1 cycloadducts, 1,2-di-tert-butyl-4,4-diphenyl-1,2-diazolidine-3,5-dione (2) and 1,3-di-tert-butyl-4,4-diphenyl-1,3-diazolidine-2,5-dione (3). The yields and spectral data are summarized in Table 1. Though little difference between the diazolidinediones 2 and 3 was found in spectral data, depression of the mixed melting point was observed. Therefore, we confirmed the structures from the fact that alkaline hydrolysis of the diazolidinedione 3 gave N-tert-butyl-N'-diphenylmethylurea.

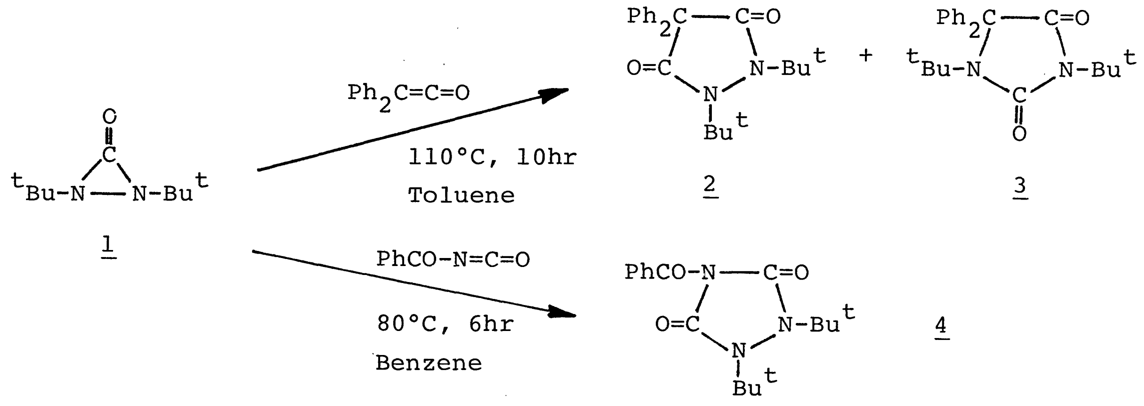
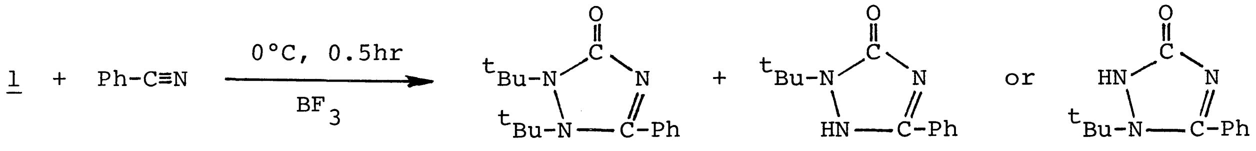


Table 1 Characterization of Cycloadducts

Adduct	Yield(%)	Mp(°C)	Ir(cm^{-1})	Mass spectrum(m/e)	Elemental analysis		
						Found	Calcd
2	26	148-	1755(C=O)	364(M^+)	C	75.53	75.79
		150	1700(C=O)	308(M^+- $Me_2C=CH_2$)	H	7.69	7.74
				194(Ph_2CCO)	N	7.50	7.69
3	32	148.5-	1760(C=O)	364(M^+)	C	75.64	75.79
		149.5	1700(C=O)	308(M^+- $Me_2C=CH_2$)	H	7.59	7.74
				194(Ph_2CCO)	N	7.61	7.69
4	73	123-	1790(C=O)	261(M^+- $Me_2C=CH_2$)	C	64.46	64.33
		125	1750(C=O)	205(M^+- $2Me_2C=CH_2$)	H	7.31	7.30
			1700(C=O)	105(PhCO)	N	13.31	13.24
5	32	157-	1675(C=O)	273(M^+)	C	70.11	70.29
		159	1545(C=N)	217(M^+- $Me_2C=CH_2$)	H	8.48	8.48
				202(217 - Me)	N	15.28	15.37
6	51	177-	3200(NH)	217(M^+)	C	66.44	66.34
		179	1675(C=O)	202(M^+- Me)	H	6.97	6.96
			1555(C=N)	161(M^+- $Me_2C=CH_2$)	N	19.51	19.34

In the reaction with benzoyl isocyanate, the 1:1 cycloadduct, 1,2-di-tert-butyl-4-benzoyl-1,2,4-triazolidine-3,5-dione (4), was merely obtained.

The cycloaddition reaction was observed not only with heterocumulenes, but with a nitrile. The reaction of the diaziridinone 1 with benzonitrile in the presence of Lewis acid gave 1:1 cycloadduct 5 and the compound 6 which might be produced from the triazolinone 5 by release of a tert-butyl group. The spectral data are shown in the table.



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REFERENCES

1) M. Komatsu, Y. Ohshiro, H. Hotta, M. Sato, and T. Agawa, J. Org. Chem., in press.
2) M. Komatsu, Y. Ohshiro, and T. Agawa, to be published.
3) M. Komatsu, Y. Ohshiro, and T. Agawa, Tetrahedron Lett., 3999 (1972).
4) F. D. Greene, J. C. Stowell, and W. R. Bergmark, J. Org. Chem., 34, 2254 (1969).

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