

PHOTOCHEMISTRY OF THE SEMICYCLIC IMIDE SYSTEM. I

EVIDENCE FOR COMPETITIVE TYPE I AND TYPE II PROCESSES¹

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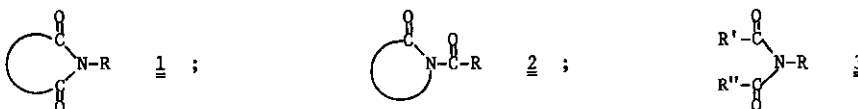
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Abstract — Photolyses of a series of N-acylpyrrolidones (4) show that semicyclic imides are capable of undergoing competitive type I and type II processes.

Imides are classified into three structural classes: cyclic 1, semicyclic 2, and noncyclic 3.² Although the photochemistry of imides has been extensively studied, most of the reports have been concerned with that of cyclic imides (1).² A recent report by Mazzocchi *et al.*,³ on the photo-reaction of "aliphatic imides" (3) which are noncyclic, prompted us to preliminarily communicate our results on the photochemistry of semicyclic imides (2).



Photolyses of a series of N-acylpyrrolidones (4) were carried out.⁴ Products were separated by preparative TLC, and the results are summarized in Table I. The mechanism for the formation of these products can be rationalized on the basis of analogy with that of the parent keto system.^{2,5} In all cases, pyrrolidone (5) may arise from α -cleavage (type I) of the carbonyl-(b) at the N-CO bond and/or type II elimination of the carbonyl-(a) (Scheme I). The ketene (6) was trapped as its ethyl ester in the reaction of 4c in an ethanol solution⁶ suggesting the occurrence of a type II(a) process "across the imide moiety"³ which directly leads to 6, though 6 could be formed also from the type I(b) process. With compound 4c, type II elimination involving the carbonyl-(b) also occurred to give 4a. Isolation of oxaloylpyrrolidone (9) (mp 139-140.5°),⁷ probably formed by coupling of the imide radical (8), supports that compound 4d undergoes type I reaction of the carbonyl-(b) (at the CO-C bond), a process favored by an adjacent methoxyl group.⁸ Generally the absence of type I(a) products may be explained by efficient reverse cyclization of possibly formed biradicals (7).

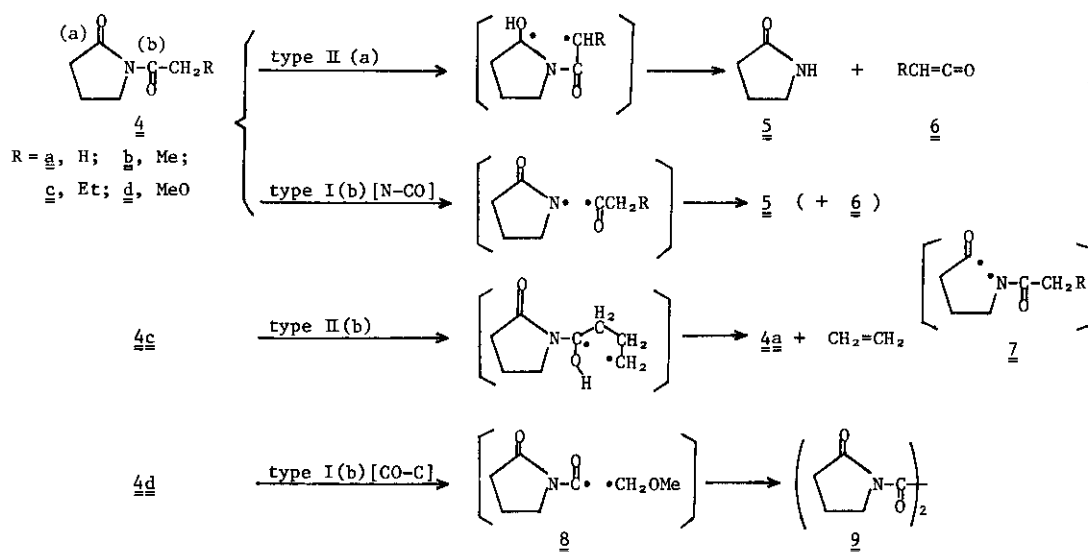
Table I Distribution of the Photoproducts from 4

Carbonyl	Reaction	Compounds isolated(%)	<u>4a</u>		<u>4b</u>	<u>4c</u>			<u>4d</u>	
			A	B	A	A	B	C*	A	B
(a)	type I		-	-	-	-	-	-	-	-
	type II	<u>5</u>	20	46	39	35	37	79	18	24
(b)	type I	<u>9</u>							12	4
	type II	<u>4a</u>	-	-	-	15	19	1	9	11

A: acetonitrile; B: t-butanol; C: ethanol

* Determined by mass chromatography

Scheme I



The above results provide the first evidence that the two carbonyls of semicyclic imides (2), endo(a) and exo(b), are both essentially photoreactive, capable of undergoing competitive type I and type II processes. Studies on the other photoreactions of the semicyclic imide system are under way.

REFERENCES AND NOTES

1. Photoinduced Reactions. 45. Part 44: Y. Kanaoka and K. San-nohe, submitted.
2. Y. Kanaoka, *Accounts Chem. Res.*, 1978, 11, 407.
3. P. H. Mazzocchi, W. Jameson, T. Nishiyama and A. DeCamp, *Tetrahedron Lett.*, 1980, 21, 989.
4. A solution (10~20 mM) was irradiated with a low-pressure 60 W mercury lamp for 1~2 hr in a stream of nitrogen.
5. N. J. Turro, "Modern Molecular Photochemistry", The Benjamin/Cummings Publishing Co., Inc., Menlo Park, California, 1978, p. 393, p. 437.
6. Ethyl butyrate ($M^+ 116$; 15 %) was detected by mass chromatography (Shimadzu-LKB 9000).
7. Identical with an authentic sample prepared by oxaloylation of pyrrolidone.
8. P. J. Wagner, *Accounts Chem. Res.*, 1971, 4, 168.

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