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INSERTION OF ETHOXYCARBONYLNITRENE INTO C-H BONDS OF CYCLIC ETHERS

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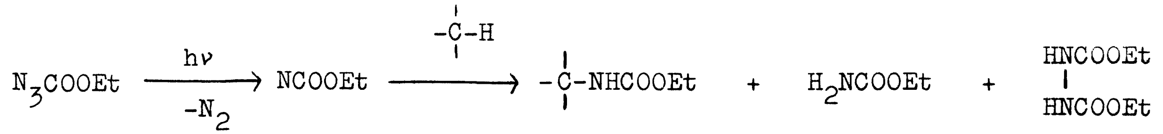
Ethyl azidoformate was photolyzed in three to six membered cyclic ethers. The α-C-H and α-methyl C-H bonds of cyclic ethers were observed to have unusually large reactivities compared with those of the corresponding C-H bonds of hydrocarbons in the insertion of ethoxycarbonylnitrene. On the anomalous reactivities, a mechanism has been advanced in which an O-N ylide is included as an intermediate of the insertion reaction.

It has been reported that ethoxycarbonylnitrene inserts exclusively into C-H bonds adjacent to ethereal oxygen in the sensitized photolysis of ethyl azidoformate with five and six membered cyclic ethers.[1)] We investigated the insertion of ethoxycarbonylnitrene into C-H bonds of several kinds of cyclic ethers.

A solution of 0.043 mole of ethyl azidoformate (I) in 0.5 mole of a cyclic ether (II) was irradiated by a low pressure mercury lamp at 0 °C under an atmosphere of nitrogen. The products were separated by vapor phase chromatography, and the structure of products was determined by means of elemental analyses and the measurements of IR and NMR spectra. The insertion products (IV) of ethoxycarbonylnitrene (III) into C-H bonds of cyclic ethers were obtained in various yields, accompanied by urethane (V) and small amounts of diethyl hydrazoformate (VI). The results obtained are shown in Table 1.



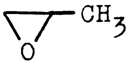
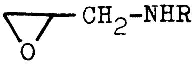
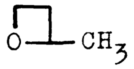
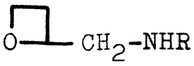
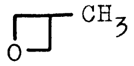
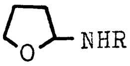
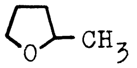
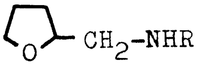
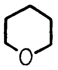
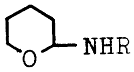
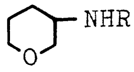
$$N_3COOEt \xrightarrow[-N_2]{h\nu} NCOOEt \xrightarrow{\begin{array}{c}|\\-C-H\\|\end{array}} \begin{array}{c}|\\-C-NHCOOEt\\|\end{array} + H_2NCOOEt + \begin{array}{c}HNCOOEt\\|\\HNCOOEt\end{array}$$

(I) (III) (IV) (V) (VI)

In the reactions with three and four membered cyclic ethers, no insertion products of III into ring C-H bonds were obtained other than those into α-methyl C-H bonds. Especially, any insertion products were recognized in the reaction with β-methyloxetane (IIc). In the reactions with five and six membered cyclic ethers, however, the nitrene inserted preferentially into ring C-H bonds at α-positions.

In the next place, the photolysis of I was carried out in a mixture of equimolar amounts of a cyclic ether and cyclohexane in order to obtain the relative reactivities of primary (1°), secondary (2°), and tertiary (3°) C-H bonds of

Table 1 Photolysis of Ethyl Azidoformate in Cyclic Ethers

Ether (II)			Product (mole %)* IV		V
(a)		(a)	 **	21	12
(b)		(b)		28	23
(c)			No insertion product		13
(d)		(d)		25	21
(e)		(e1)		6.1	34
		(e2)		12	
(f)		(f1)		25	16
		(f2)		4.8	

* Calculated based on the azide used. ** R : $-COOC_2H_5$

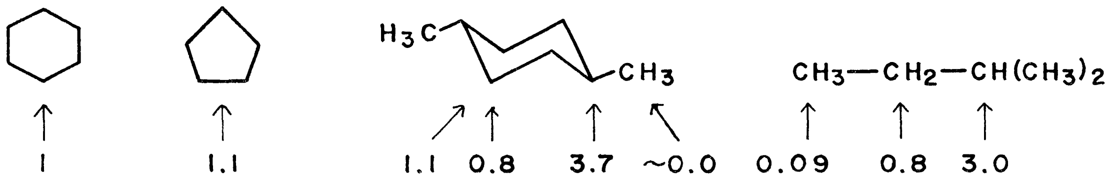
Table 2 Relative Reactivities

	Insertion product (mole %) IV	Insertion product (mole %) cyc-$C_6H_{11}NHR$	Type of C-H bond	Relative reactivity per C-H bond of cyclohexane
(a)	15.0	11.3	1° (α-CH_3)	5.6 (± 0.2)*
(b)	16.8	6.9	1° (α-CH_3)	9.8 (± 0.1)
(d)	18.1	10.8	2° (Ring-α)	5.0 (± 0.1)
(e1)	2.3	7.0	1° (α-CH_3)	1.3 (± 0.1)
(e2)	6.9		3° (Ring-α)	11.7 (± 1.1)
(f1)	13.3	13.5	2° (Ring-α)	3.0 (± 0.2)
(f2)	2.6		2° (Ring-β)	0.6 (± 0.1)

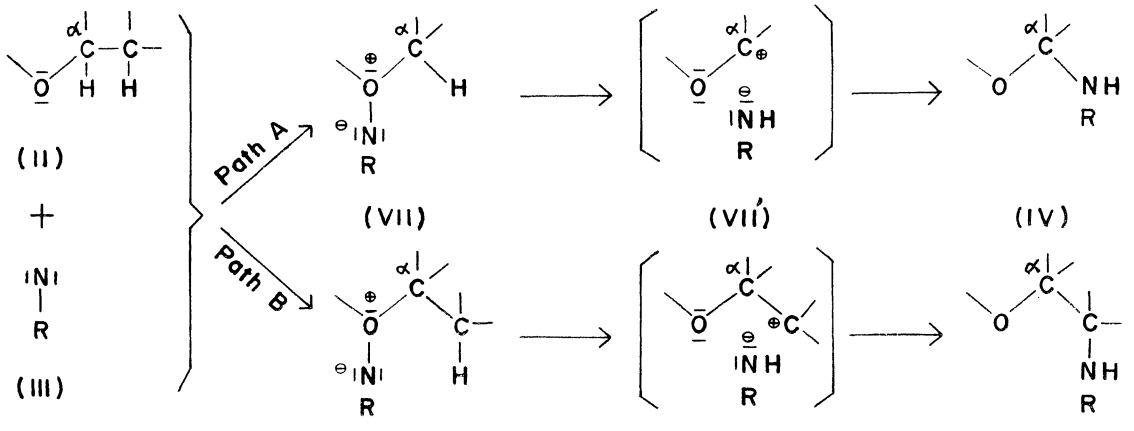
* The relative errors appear in parentheses.

cyclic ethers to one C-H bond of cyclohexane. As is shown in Table 2, the reactivities of α-C-H and α-methyl C-H bonds of cyclic ethers were found to be larger than those of C-H bond of cyclohexane, except the case of tetrahydropyran (IVf2).

The results are quite different from those obtained in the photolysis of I in cyclic and acyclic hydrocarbons. In the reactions in hydrocarbons, the relative reactivities of primary, secondary, and tertiary C-H bonds of cyclic hydrocarbons toward ethoxycarbonylnitrene were observed to be $1^\circ \ll 2^\circ < 3^\circ$, and their values were almost the same to those of the corresponding C-H bonds of acyclic hydrocarbons.2)



Therefore, the insertion in question must have proceeded by another mechanism than that proposed in the reaction with hydrocarbons.3,4) The mechanism of the insertion of nitrene into α-C-H and α-methyl C-H bonds of cyclic ethers may reasonably be explained as follows. The nitrene (III) co-ordinates with its nitrogen atom to ethereal oxygen giving an intermediate ylide (VII) ; the O-N bond of the ylide is not so strong that the ylide converts into IV through the transition state (VII').



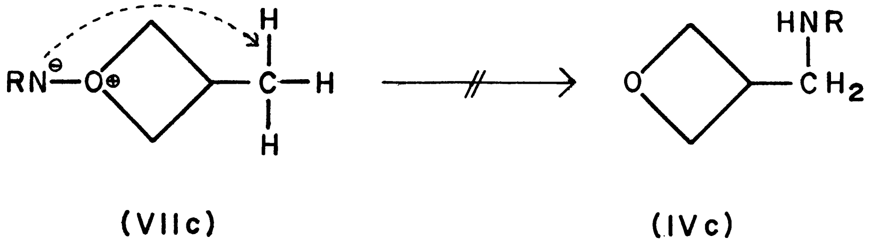
R : -COOC$_2$H$_5$

Path A Insertion into α-C-H bonds

Path B Insertion into α-metnyl C-H bonds

Scheme

In the cases of small ring ethers (IIa and IIb), a positive charge would be hardly created on the α-carbon atom in the transition state, since the bond angles of rings are strained to some extent, resulted in failure to the formation of insertion products into ring C-H bonds. In the case of β-methyloxetane (IIc), the distance between the nitrogen atom of the ylide (VIIc) and a methyl C-H bond seems to be too far to give IVc.



Scheme 2

The insertion product (IVf2) might be formed not by the ylide mechanism, but by the one-step mechanism proposed in the reaction of nitrene with hydrocarbons, judging from the reactivity of β-C-H bonds of pyran (IIf).

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