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FORMATION OF N-ALKOXYURETHANES IN THE REACTION OF ETHOXYCARBONYLNITRENE WITH ETHERS

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The photolysis of ethyl azidoformate in ethers gave N-alkoxyurethanes accompanied by ethoxycarbonylaminoethers, insertion products of ethoxycarbonylnitrene into the C-H bonds of ethers. The formation of N-alkoxyurethanes gives a support to a mechanism in which an O-N ylide is included as an intermediate of α-C-H insertion reaction.

In a previous communication,[1] we reported that the α-C-H and α-methyl C-H bonds of cyclic ethers showed 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. In this paper, we wish to report on the formation of N-alkoxyurethanes, which seems to give a support to the O-N ylide mechanism.

The photolysis of ethyl azidoformate (I, 0.025 mole) in ethers (II, 0.5 mole) gave N-alkoxyurethanes (III) in addition to ethoxycarbonylaminoethers (IV), insertion products of ethoxycarbonylnitrene into the C-H bonds of ethers, and urethane (V). The yields of products are summarized in Table 1. The products (III) were identified by comparison with the N-alkoxyurethanes obtained by the insertion of ethoxycarbonylnitrene into the O-H bonds of the corresponding alcohols[2] (Table 2).

Table 1. Photolysis of Ethyl Azidoformate in Ethers

R-O-R (II) R	Product (%)* RONHCOOEt (III)		IV		$H_2NCOOEt$ (V)
Ethyl	(a)	3.9	$CH_3\text{-}CH(NHCOOEt)\text{-}OC_2H_5$	31	17
n-Propyl	(b)	5.6	$CH_3CH_2\text{-}CH(NHCOOEt)\text{-}OC_3H_7$	32	20
			$CH_3\text{-}CH(NHCOOEt)\text{-}CH_2OC_3H_7$	3.1	
n-Butyl	(c)	4.1	$CH_3CH_2CH_2\text{-}CH(NHCOOEt)\text{-}OC_4H_9$	25	17
			$CH_3CH_2\text{-}CH(NHCOOEt)\text{-}CH_2OC_4H_9$	3.8	
			$CH_3\text{-}CH(NHCOOEt)\text{-}CH_2CH_2OC_4H_9$	3.9	
iso-Amyl	(d)	2.4	$(CH_3)_2CHCH_2\text{-}CH(NHCOOEt)\text{-}OC_5H_{11}$	17	15
			$(CH_3)_2C(NHCOOEt)\text{-}CH_2CH_2OC_5H_{11}$	5.7	

* Yields based on the azide used.

The relative reactivities of various types of C-H bonds of ethers per C-H bond of cyclohexane were estimated[1] based on the yields of insertion products of ethoxycarbonylnitrene into C-H bonds in the photolysis of I (0.025 mole) in an equimolar mixture of an ether (0.25 mole) and cyclohexane (0.25 mole). The estimated values are listed in Table 3, and those of primary (1°), secondary (2°), and tertiary (3°) C-H bonds in 2-methylbutane are also shown for the sake of comparison. As is shown in Table 3, the values of ethereal 2° (β-C-H) and 3° (γ-C-H) bonds are almost the same to those of the corresponding C-H bonds of 2-methylbutane, respectively, while the values of 2°(α-C-H) bonds of ethers are 5.5 times as large as those of 2° C-H bond of 2-methylbutane.

Table 2. NMR and IR Data of N-Alkoxyurethanes (III)

III	NMR (τ) in CCl_4	IR (cm^{-1}) in CCl_4 NH	C=O	C—O
(a)	CH_3—CH_2—ONH—COO—CH_2—CH_3 8.70 6.14 1.97 5.85 8.73 (t) (q) (bs) (q) (t)	3300	1720	1240 1105
(b)	CH_3—CH_2—CH_2—ONH—COO—CH_2—CH_3 9.03 8.37 6.25 2.00 5.86 8.71 (t) (six) (t) (bs) (q) (t)	3280	1720	1255 1125
(c)	CH_3—CH_2—CH_2—CH_2—ONH—COO—CH_2—CH_3 9.05 8.2~8.9 6.22 1.97 5.86 8.71 (t) (m) (t) (bs) (q) (t)	3280	1725	1260 1125
(d)	$(CH_3)_2$>CH—CH_2—CH_2—ONH—COO—CH_2—CH_3 9.06 8.1~8.6 6.18 2.08 5.85 8.71 (d) (m) (t) (bs) (q) (t)	3320	1730	1260 1120

Table 3. Relative Reactivities per C-H Bond of Cyclohexane

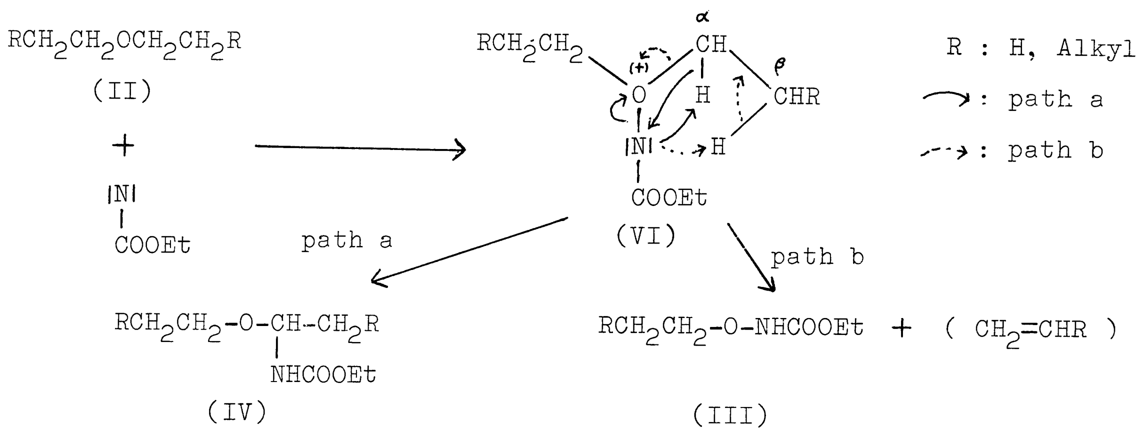
Run	Ether 2°(α-C-H)	Ether 2°(β-C-H)	Ether 3°(γ-C-H)	Cyclohexane 2°	2-Methylbutane 1°	2-Methylbutane 2°	2-Methylbutane 3°
A	4.5	0.7		1			
B	4.4		2.9	1			
C				1	0.09	0.8	3.0

A) Reaction in a mixture of n-butylether and cyclohexane.

B) Reaction in a mixture of iso-amylether and cyclohexane.

C) Reaction in a mixture of 2-methylbutane and cyclohexane.

The mechanism of the formation of N-alkoxyurethanes (III) and α-C-H insertion products of ethoxycarbonylnitrene may reasonably be explained by assuming a common O-N ylide intermediate (VI) as follows.



When the nitrogen atom of VI migrates to α-carbon atom taking with α-hydrogen abstraction, α-C-H insertion products may be given (path a). If the nitrogen atom abstracts β-hydrogen followed by O-C bond cleavage, N-alkoxyurethanes may be produced (path b). The formation of III seems to give a support to the O-N ylide mechanism of α-C-H insertion reaction. In the reaction of ethoxycarbonylcarbene with n-butyl ether, the formation of ethyl n-butoxyacetate and 1-butene has been observed[3]. The O-C bond cleavage of ether by the carbene also is explained in terms of an analogous ylide mechanism[4].

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