

REACTION OF N,N-DICHLOROURETHAN WITH ETHERS.  
A NOVEL CLEAVAGE-CHLORINATION REACTION

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The reaction of alkoxy radicals with the  $\alpha$ -hydrogen atoms of ethers, acetals and ketals is well documented in the literature (1,2,3). The resulting  $\alpha$ -alkoxyalkyl radical undergoes a variety of reactions, the most common of which are chain transfer (substitution), fragmentation and dimerization, with the first predominating by far. A few instances have been recorded, however, where a minor amount of the highly reactive  $\alpha$ -alkoxyalkyl radical undergoes homolytic  $\beta$ -scission to yield a carbonyl compound (3,4). A recent report on the reaction of t-butyl hypochlorite with ethers (5) has prompted us to describe the results of the reaction of ethers with N,N-dichlorourethan (DCU) to produce novel cleavage-chlorination products containing the carbamate function.

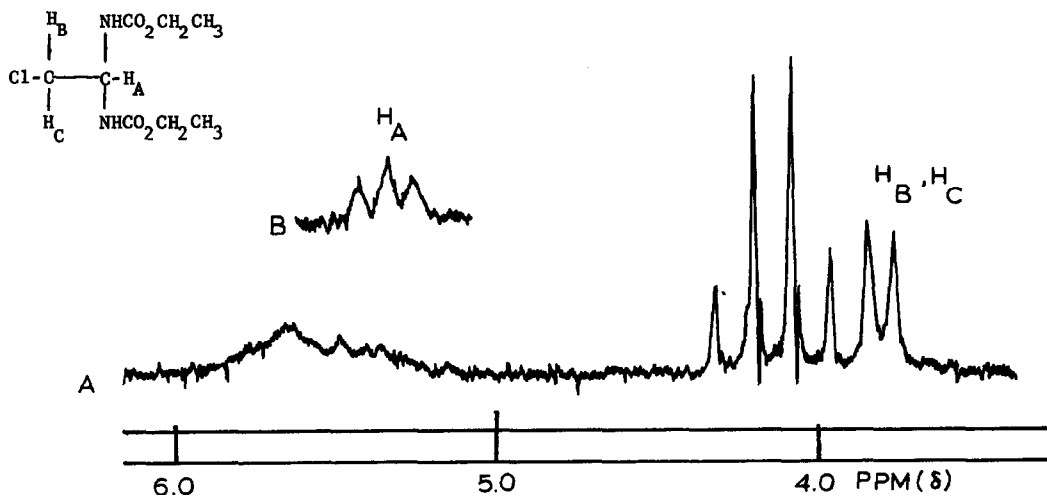
Interaction of a benzene solution of two moles of DCU (I) with one mole of diethyl ether (II) at 80° for three hours, yields a single crystalline product (III), m.p. 145-147°, in 75% yield.



The structure of III,  $\text{C}_8\text{H}_{15}\text{ClN}_2\text{O}_4$ , was determined to be the dicarbamate of  $\alpha$ -chloroacetaldehyde from spectral data. Its infrared spectrum showed  $\nu_{\text{max}}^{\text{CHCl}}$  at 3450 (NH),

1730 (carbonyl) and  $1530\text{ cm}^{-1}$  (amide II), all suggestive of a carbamate structure. The relevant portion of the NMR spectrum ( $\text{CDCl}_3$ ) of III, taken on a Varian A-60 spectrometer is shown in Fig. 1. The methyl protons (6H) appears as an expected triplet centered at 1.24 ppm. (TMS internal standard). The methylene protons (4H) are seen as a quartet centered at 4.14 ppm. Protons  $\text{H}_B$  and  $\text{H}_C$  (2H) are seen as a doublet ( $J=5\text{ cps}$ ) centered at 3.78 ppm. The proton  $\text{H}_A$  overlaps with the N-H protons and all appear as a broad multiplet centered at 5.58 ppm (3H). Treatment of III with deuterium oxide and a drop of trifluoroacetic acid exchanges the proton on each of the nitrogen atoms by deuterium, and the spectrum (Fig. 1,B) now displays  $\text{H}_A$  as an anticipated triplet ( $J=5\text{ cps.}$ ) centered at 5.38 ppm (1H) and broadened by the quadripole of nitrogen.

Fig. 1



A) NMR spectrum of reaction product of DCU and diethyl ether

B) After treatment with  $\text{D}_2\text{O}$  and trace of  $\text{CF}_3\text{CO}_2\text{H}$

The reaction was then further investigated with the next three higher homologous symmetrical *n*-dialkyl ethers and also with dibenzyl ether. With all the alkyl ethers the major product is the  $\alpha$ -chloro bis-carbamate, while with benzyl ether the product is the bis-carbamate derivative of benzaldehyde. The yields of analytically pure bis-carbamates are in the range of 60-80%. Re-

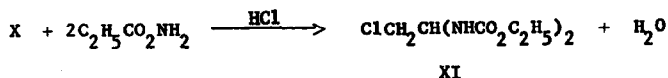
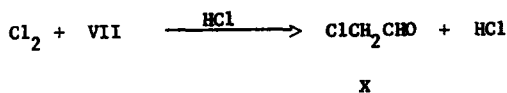
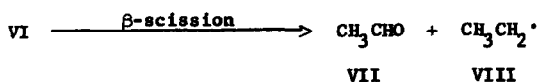
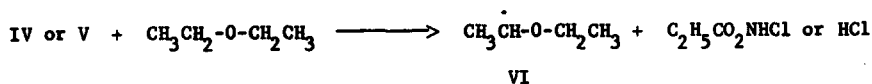
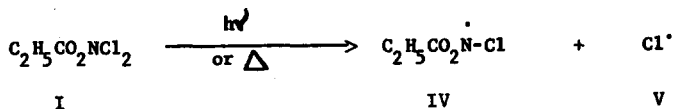
sults are summarized in Table I.

TABLE I  
Reaction of DCU With Alkyl Ethers At 80°<sup>a,b</sup>

<u>Ether</u>	<u>Reaction Time Hrs.</u>	<u>Product<sup>c</sup></u>	<u>M.P. °C</u>	<u>Yield<sup>d</sup></u>
Diethyl	2	$\text{ClCH}_2\text{CH}(\text{NHCO}_2\text{C}_2\text{H}_5)_2$ (XI)	144-147°	75
Di-n-propyl	2	$\text{CH}_3\text{CHClCH}(\text{NHCO}_2\text{C}_2\text{H}_5)_2$	111-112°	68
Di-n-butyl	1	$\text{CH}_3\text{CH}_2\text{CHClCH}(\text{NHCO}_2\text{C}_2\text{H}_5)_2$	122-122.5°	82
Di-n-pentyl	2	$\text{CH}_3(\text{CH}_2)_2\text{CHClCH}(\text{NHCO}_2\text{C}_2\text{H}_5)_2$	106-107°	58
Dibenzyl	0.5	$\text{C}_6\text{H}_5\text{CH}(\text{NHCO}_2\text{C}_2\text{H}_5)_2$	169-170°	62

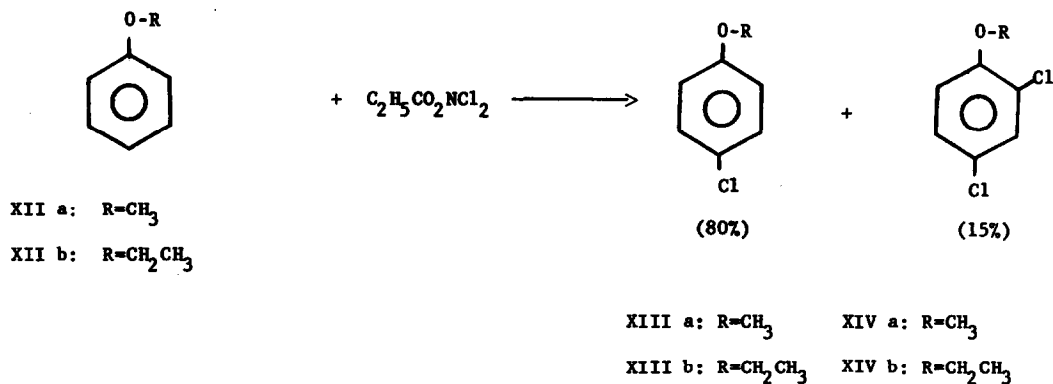
a) With benzene as solvent. b) Molar ratio of DCU to ether, 2:1. c) All products gave satisfactory elemental analyses. d) Analytically pure, based on ether.

To account for the observed products the following reaction sequences are proposed, using diethyl ether as a prototype. In the addition of DCU to monoolefinic compounds (6) we had previously suggested that the initiation step involves the homolytic scission of a nitrogen-chlorine bond of a DCU molecule to generate an N-chlorocarboethoxy radical (IV) and a chlorine atom (V). The radical (IV) or a chlorine atom (V) abstracts an  $\alpha$ -hydrogen of the ether to generate the  $\alpha$ -alkoxyalkyl radical (VI) followed by rupture of the  $\beta$ -carbon-oxygen bond to yield the corresponding aldehyde (VII) and the alkyl radical (VIII). The alkyl radical then abstracts a chlorine atom from another molecule of DCU or from molecular chlorine to give the radical (IV) or (V) and an alkyl chloride (IX), which can be shown to be present in the crude reaction mixture by glpc. Chlorination of the aldehyde is effected either by chlorine or by abstraction of the  $\alpha$ -hydrogen of the aldehyde by radical (IV) or a chlorine atom (V), followed by reaction with another molecule of DCU. We have excluded the radical pathway by observing that reaction of DCU with aldehydes does not give  $\alpha$ -chlorination but rather oxidation to the corresponding acid. The final step involves the acid-catalyzed condensation of the chloro aldehyde with urethan (7). Urethan and chlorine are readily formed by reaction of the hydrogen chloride generated with mono- or dichlorourethan. In the case of dibenzyl ether, the benzaldehyde formed condenses with urethan.



The facile high-yield formation of high melting crystalline products suggests the reaction of DCU with n-symmetrical dialkyl ethers as a convenient derivatization-identification method. When the reaction was extended to two mixed alkyl-aromatic ethers, anisole (XIIa) and phenetole (XIIb), a totally different result was obtained. In contrast to the results of Walling and Mintz (5) who studied reactions of *t*-butyl hypochlorite with XIIb, where the  $\alpha$ -chloro ether is the major product, the products we isolated in both instances in yields exceeding 90% were the ring chlorinated products, XIII and XIV. These results are analogous to those obtained in the reaction of aromatic ethers with *N*-bromosuccinimide (8).

Reaction of DCU with ethyl vinyl ether gave the same chlorination-cleavage product as with diethyl ether; no double bond addition was observed.



In summary, the reaction of DCU with di-*n*-alkyl ethers has been investigated, and the major product in all cases arises from  $\beta$ -scission of the intermediate  $\alpha$ -alkoxyalkyl radical. Alkyl-aryl ethers undergo ring chlorination. Further work is being carried out in this laboratory on the reaction of *N,N*-dichlorourethan with other classes of compounds containing reactive hydrogen atoms; results will be reported at a future date.

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