

DIRECT CONVERSION OF ETHERS TO ESTERS  
BY TRICHLOROISOCYANURIC ACID

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The direct oxidation of ethers of formula  $R-CH_2-O-R'$  has been reported<sup>1</sup> to give alcohols, acids and carboxylates when effected with molecular oxygen. There seems to be no general laboratory method for conversion of ethers to esters in good yield. We are unable to find any report of the use of N-halogen compounds or hypohalites for direct conversion of diethyl ether or other aliphatic ethers to esters. Benzyl ethers have been reported to undergo oxidative cleavage to yield benzaldehydes on treatment with NBS and other oxidizing agents.<sup>2</sup>

We wish to report the production of carboxylic acid esters directly from ethers of formula  $R-CH_2-O-R'$  by the use of trichloroisocyanuric acid (1) in the presence of an excess of water.

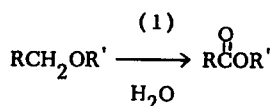
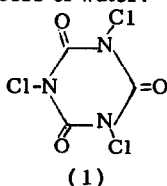


TABLE 1: SUMMARY OF OXIDATION REACTIONS

<u>R</u>	<u>R</u>	<u>Reaction Conditions (3°C)<sup>3</sup></u>	<u>Major Product and Yield<sup>4</sup></u>	<u>Minor Products</u>
CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	Stir 3 hr., excess Et <sub>2</sub> O	CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub> , 49%	None
n-C <sub>3</sub> H <sub>7</sub>	n-C <sub>4</sub> H <sub>9</sub>	Stir 20 hr., excess Bu <sub>2</sub> O <sup>5</sup>	C <sub>3</sub> H <sub>7</sub> COOC <sub>4</sub> H <sub>9</sub> , 100%	None
C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	Stir 15 hr., sl. excess of ØCH <sub>2</sub> OC <sub>2</sub> H <sub>5</sub>	ØCHO, 53% <sup>6</sup>	ØCOOC <sub>2</sub> H <sub>5</sub> , 4.7%

Table 1 shows the results of some preliminary work. All reactions were run in the presence of a quantity of water equal to or slightly greater than three times the molar amount of (1) present. Thus, if 0.05 moles (1) were used, 0.15-0.20 moles water were included in the reaction mixture.

In another experiment, it was found we were able to convert benzyl alcohol to benzaldehyde in 53.7% yield by reaction with trichloroisocyanuric acid in the presence of an excess of water. It is noted in Table 1 that benzyl ethyl ether produced benzaldehyde as its major product. It is interesting that this reagent (i.e., trichloroisocyanuric acid), which generates esters from ethers, will, under the same conditions, oxidize benzyl alcohol no further than benzaldehyde.

Extensive work on related reactions is presently being done.

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- (3) The  $\text{Bu}_2\text{O}$  reaction was stirred for 12 hours at  $3^\circ$ : It was then allowed to warm to  $20^\circ$  and stirring was continued at that temperature for eight hours.
- (4) Values for yields are based on the number of moles of trichloroisocyanuric acid (the ether and the water were always in excess).
- (5) In this reaction, an 18 fold molar excess of water was used.
- (6) This value is based on the conversion of benzyl ethyl ether to benzaldehyde and ethyl alcohol.