Reactions of Trichloroacetyl Isocyanate with Unsaturated Ethers

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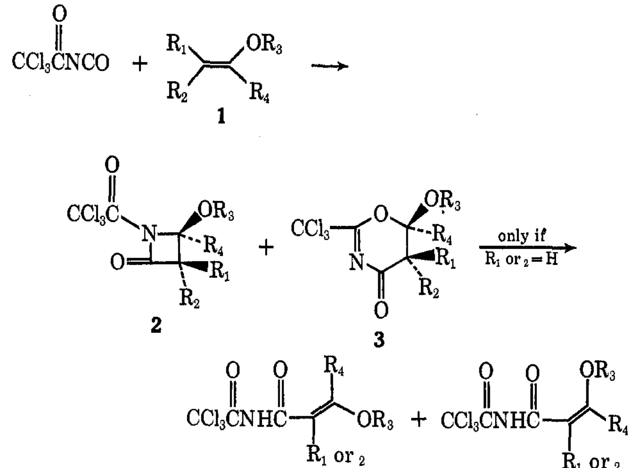
The reaction of trichloroacetyl isocyanate with unsaturated ethers gave 1:1 adducts. In most of these reactions the adducts, 3-alkoxy-*N*-(trichloroacetyl)acrylamides (**4** and **5**), were linear; however, both four- and six-membered cyclic intermediates, 3-alkoxy-1-(trichloroacetyl)-2-azetidinones (**2**) and 6-alkoxy-5,6-dihydro-2-(trichloromethyl)-4*H*-1,3-oxazin-4-ones (**3**), were observed by infrared and nmr spectroscopy. The initially formed mixture of intermediates **2** and **3** went smoothly to linear product. The four-membered-ring intermediate **2** opened to the linear product *via* **3**. The cyclic intermediates appear to be formed stereospecifically, and the observed rate enhancement with increasing solvent polarity suggests polar transition states for the formation of both cyclic intermediates and linear products.

The reaction of unsaturated ethers with ketenes has been shown to yield four-membered-ring 1:1 adducts.[1] The highly reactive arylsulfonyl isocyanates were reported by Effenberger and Gleiter to react with unsaturated ethers to give 1:1 adducts, either cyclic or linear depending upon reaction conditions and structure of the ethers.[2a] These authors indicated that acyl isocyanates do not react with unsaturated ethers. Our studies show that trichloroacetyl isocyanate does react with unsaturated ethers to give 1:1 adducts **4**,[3] by way of cyclic intermediates **2** and **3**.[4]



a, $R_{1,2,4} = H;\ R_3 = C_2H_5$

b, $R_{2,4} = H;\ R_{1\ \text{and}\ 3} = (CH_2)_3$

c, $R_{1,2} = CH_3;\ R_4 = H;\ R_3 = C_2H_5$

d, $R_1 = CH_3;\ R_{2,4} = H;\ R_3 = C_2H_5$

e, $R_2 = CH_3;\ R_{1,4} = H;\ R_3 = C_2H_5$

f, $R_{1,2,3} = CH_3;\ R_4 = OCH_3$

g, $R_{1,2} = H;\ R_3 = C_2H_5;\ R_4 = OC_2H_5$

We found that the behavior of acyl isocyanates with unsaturated ethers parallels that of arylsulfonyl isocyanates; therefore, our work confirms that of Effenberger[2b] and extends it to isocyanates activated by certain acyl groups.

Infrared and nmr spectroscopy were employed to monitor the course of the reaction and to assign structures to the cyclic intermediates. Preparative runs readily gave the linear products in good yield.

Ethyl vinyl ether (**1a**) and trichloroacetyl isocyanate reacted vigorously. If the temperature was allowed to rise to *ca.* 50°, a 77% yield of 3-ethoxy-*N*-(trichloroacetyl)acrylamide (**4a**) resulted; however, when these same reagents were combined at room temperature in deuteriochloroform, the reaction gave complete conversion to 6-ethoxy-5,6-dihydro-2-(trichloromethyl)-4*H*-1,3-oxazin-4-one (**3a**). No four-membered-ring intermediate **2a** was detected, even when the reaction was run at $-45°$. That the structure of the intermediate was **3a** and not the 1,2 cycloadduct **2a** was established from its infrared spectrum. In carbon tetrachloride solution, **3a** exhibited maxima at 5.75 (C=N) and 6.21 μ (C=O). If the compound were **2a**, it would be expected to show a maximum at shorter wavelength for the strained-ring carbonyl, since Effenberger and Gleiter[2a] found that the carbonyl in analogous sulfonyl compounds absorbed at about 5.54–5.59 μ. Ethyl vinyl ether also reacted with benzoyl isocyanate to form the linear product *N*-(3-ethoxyacryloyl)benzamide. No effort was made to detect intermediate products.

Benzoyl isocyanate did not react with 3,4-dihydro-2*H*-pyran (**1b**) in refluxing benzene, but trichloroacetyl isocyanate reacted at room temperature to give a 74% yield of 3,4-dihydro-*N*-(trichloroacetyl)-2*H*-pyran-5-carboxamide (**4b**). When the reaction was run in carbon tetrachloride at room temperature and monitored by nmr, the starting materials rapidly formed approximately equal amounts of **2b** and **3b**. The four-membered cyclic intermediate decayed into **3b**, so that at one point during the reaction **3b** was the sole species present. Then **3b** slowly opened to give **4b**.

Trichloroacetyl isocyanate and ethyl 2-methylpropenyl ether (**1c**) gave 80–87% yields of a mixture of **2c** and **3c** in carbon tetrachloride or acetonitrile. Initially, about 60% of the mixture was **2c**, but **3c** rapidly became predominant in acetonitrile solution. The linear product was not formed, since neither R_1 nor R_2 was hydrogen.

Both *cis*- and *trans*-ethyl propenyl ether (**1d** and **1e**) reacted with trichloroacetyl isocyanate in carbon tetrachloride to form four- and six-membered-ring intermediates. The cis isomer **1d** gave the intermediates assigned as **2d** and **3d**, whereas the trans isomer **1e** gave

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[1] R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, **29**, 1239 (1964), and references contained therein.

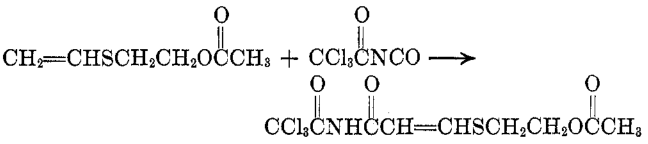
[2] (a) F. Effenberger and R. Gleiter, *Chem. Ber.*, **97**, 1576 (1964); (b) F. Effenberger and G. Kiefer, *Angew. Chem., Int. Ed. Engl.*, **6**, 95 (1967).

[3] As this paper was being prepared, Speziale and coworkers [L. R. Smith, A. J. Speziale, and J. E. Fedder, *J. Org. Chem.*, **34**, 633 (1969)] reported that chloroacetyl isocyanate and dihydropyran gave a linear 1:1 adduct in low yield. They did not detect any cyclic intermediates. Effenberger and Gleiter[2a] had previously reported that benzoyl isocyanate and unsaturated ethers did not react.

[4] Cyclic products analogous to **2** and **3** were recently reported for the addition of α,β-dialkoxy-substituted olefins and acyl isocyanates: R. Lattrell, *Justus Liebigs Ann. Chem.*, **722**, 142 (1969).

two different intermediates **2e** and **3e**. For each reaction, the six-membered-ring intermediate was the major species formed, and the four-membered-ring intermediate decayed slowly into the six-membered-ring intermediate. Furthermore, the trans intermediate **2e** rearranged to **3e**, and **3e** rearranged into the cis intermediates **2d** and **3d**. After 2–5 days, two linear products **4d** and **5d** began to form. The ratio of **4d**:**5d** (7:3) remained fairly constant until all cyclic intermediates were consumed; however, after an additional week at room temperature the ratio had reversed.

The vinyl thioether, 2-(vinylthio)ethyl acetate, reacted like vinyl ethers **1a–d** with trichloroacetyl isocyanate; it gave a linear 1:1 adduct **6**.

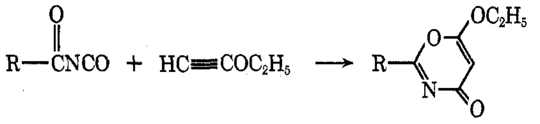


$$CH_2{=}CHSCH_2CH_2O\overset{\overset{O}{\|}}{C}CH_3 + CCl_3\overset{\overset{O}{\|}}{C}NCO \longrightarrow CCl_3\overset{\overset{O}{\|}}{C}NH\overset{\overset{O}{\|}}{C}CH{=}CHSCH_2CH_2O\overset{\overset{O}{\|}}{C}CH_3$$

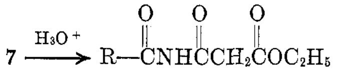
6

Scarpati and coworkers reported that phenyl isocyanate reacted with disubstituted ketene acetals to form four-membered-ring 1:1 cycloadducts, with monosubstituted ketene acetals to form linear 1:1 adducts, and with unsubstituted ketene acetals to form six-membered-ring 2:1 cycloadducts.[5] In general, we found that the reactions of trichloroacetyl isocyanate with ketene acetals did not parallel those of phenyl isocyanate. Trichloroacetyl isocyanate and dimethylketene dimethyl acetal (**1f**) gave a 1:1 adduct in quantitative yield tentatively assigned as the six-membered-ring compound **3f**. Since the adduct was hydrolyzed rapidly by moisture in the air, isolation was difficult. Unsubstituted ketene acetal (**1g**) and trichloroacetyl isocyanate gave the linear 1:1 adduct, 3,3-diethoxy-*N*-(trichloroacetyl)acrylamide (**4g**). No cyclic intermediates were observed by nmr, even at −45° in deuteriochloroform.

The reaction of ethyl ethynyl ether with trichloroacetyl isocyanate gave 6-ethoxy-2-(trichloromethyl)-4*H*-1,3-oxazin-4-one (**7a**) in quantitative yield and with benzoyl isocyanate gave 6-ethoxy-2-phenyl-4*H*-1,3-oxazin-4-one (**7b**) in 85% yield. The structure of the 1,4 cycloaddition product **7** was assigned from nmr and ir spectra and from hydrolysis and hydrogenation. The hydrolysis of **7a** in acetonitrile containing moist formic acid gave ethyl *N*-(trichloroacetyl)malonamate (**8a**) in quantitative yield. The hydrolysis of **7b** under the same conditions or with dilute aqueous hydrochloric acid gave ethyl *N*-benzoylmalonamate (**8b**). Hydrogenation of **7b** over palladium on carbon gave ethyl *N*-benzylmalonamate (**9**) in 83% yield.

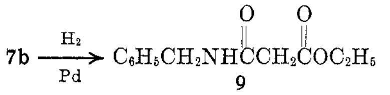


7a, R = CCl_3
b, R = C_6H_5



$$7 \xrightarrow{H_3O^+} R\overset{\overset{O}{\|}}{C}NH\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}OC_2H_5$$

8a, R = CCl_3
b, R = C_6H_5



$$\mathbf{7b} \xrightarrow[Pd]{H_2} C_6H_5CH_2NH\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}OC_2H_5$$

9

The reaction of 1-buten-3-ynyl methyl ether with trichloroacetyl isocyanate resulted in a cycloaddition involving only the acetylenic bond to give 6-(2-methoxyvinyl)-2-(trichloromethyl)-4*H*-1,3-oxazin-4-one (**10**).

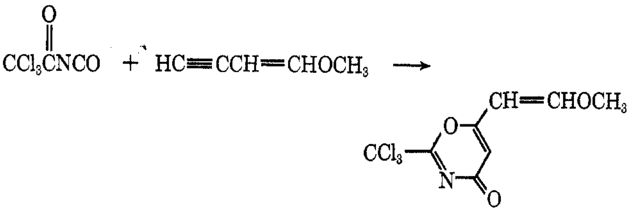


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Table I presents the initial ratios of the intermediates and the approximate reaction half-lives for the formation of cyclic intermediates and linear products. Both acetonitrile and carbon tetrachloride were used as solvents in order to obtain convenient reaction rates and to ascertain the effects of solvent polarity. The reaction pathway and the initial ratios of intermediates were virtually the same for both solvent systems. The rate of disappearance of unsaturated ether was about 350 times faster in acetonitrile than in carbon tetrachloride.

TABLE I

INITIAL RATIOS OF INTERMEDIATES AND REACTION HALF-LIVES[a] AT 30° FOR TRICHLOROACETYL ISOCYANATE AND UNSATURATED ETHERS

Ether	Initial ratio of **2**/**3**	$T_{1/2}$ for disappearance of ether in CCl_4,[b] min	$T_{1/2}$ of **2** → **3** in CH_3CN, hr	$T_{1/2}$ of **3** → **4**[c] in CCl_4, days
1a	0/1	5		1
1b	1/1	90	<0.5[d]	2
1c	3/2	120	18[e]	
1d	1/4	1	...[f]	6[g]
1e	1/4	10	...[f]	6[g]
1g	Linear adduct only	...[h]		
Ethyl ethynyl ether	0/1	<0.5		

[a] For all systems, [acyl isocyanate] was *ca.* 0.8 *M*; [ether] was *ca.* 0.5 *M*. [b] In CH_3CN, ether was always consumed in 30 sec or less. Rate was *ca.* 350 times faster in CH_3CN. [c] In all systems but dihydropyran, all **2** went to **3** before any linear product was detected; therefore, $T_{1/2}$ was taken as the time from complete disappearance of **1** until half of **4** was formed. [d] $T_{1/2}$ (CCl_4) = *ca.* 5 hr. [e] The rearrangement of **2** to **3** in CCl_4 was too slow for convenient measurement. [f] This system was relatively stable to the **2** to **3** conversion. The conversion of trans products to cis products had a $T_{1/2}$ of *ca.* 5 days in CCl_4. [g] $T_{1/2}$ of *ca.* 1 day in CH_3CN. [h] Too fast to measure.

The increase in reaction rate with increasing solvent polarity indicates that a polar species is involved in the

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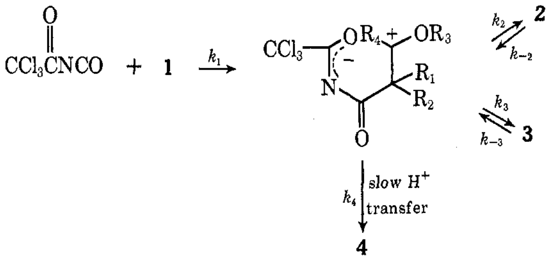
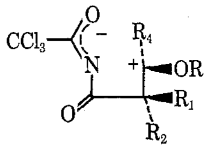
[5] (a) R. Scarpati, *Rend. Accad. Sci. Fis. Mat.* (*Soc. Naz. Sci. Napoli*), [4] **25**, 7 (1958); *Chem. Abstr.*, **55**, 11423 (1961). (b) R. Scarpati, G. Del Re, and T. Maone, *Rend. Accad. Sci. Fis. Mat.* (*Soc. Naz. Sci. Napoli*), [4] **26**, 26 (1959); *Chem. Abstr.*, **55**, 11423 (1961). (c) R. Scarpati and R. A. Nicolaus, *Rend. Accad. Sci. Fis. Mat.* (*Soc. Naz. Sci. Napoli*), [4] **29**, 154 (1962).

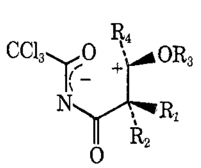
formation of these cyclic intermediates[6,7] and in the conversion of **2** to **3**. A probable reaction pathway is illustrated below where $k_1 \geq k_2 > k_3$, $k_{-2} > k_{-3}$, both k_2 and $k_3 > k_{-2}$ and k_{-3}, and all the above k's $> k_4$.



The initial ratio of four-membered-ring intermediate **2** to six-membered-ring intermediate **3** is probably determined largely by the initial conformation of the zwitterion, with orientation A leading to **2** and B to **3**.



A



B

The cycloaddition reactions appear to be stereospecific, since only one isomer of each cyclic intermediate was detected, and, more critically, *trans*-ethyl propenyl ether (**1e**) gave two distinct, cyclic intermediates, one six-membered and one four-membered, which changed to the two different cyclic intermediates obtained from *cis*-ethyl propenyl ether (**1d**). Cis addition to the unsaturated ethers is assumed, but there is no unequivocal proof. One might have anticipated that the cyclic products from *trans*-ethyl propenyl ether (**1e**) would be more stable than those from the cis isomer; however, sulfonyl isocyanates are reported to react with *cis*- and *trans*-methyl propenyl ethers to give compounds analogous to **2d** and **2e** *via* stereospecific *cis* additions where the product corresponding to **2d** is only 0.27 kcal/mol less stable than the one analogous to **2e**.[7]

The ethyl propenyl ethers gave two isomeric, linear products **4d** and **5d**, the relative amount of **4d** decreasing with time. The thermodynamic preference for **5d** may be due to this isomer's ability to H bond between the N-H and ethoxy oxygen.

In summary, although the relative magnitudes of k_1–k_4 vary somewhat from one unsaturated ether system to another, the trend of the rates appears to be the same. The rate enhancement with increasing solvent polarity suggests polar transition states, but the subtle features controlling the magnitude of the rates are not apparent at this time. The cyclic intermediates appear to be formed stereospecifically.

Experimental Section

Trichloroacetyl isocyanate,[8,9] benzoyl isocyanate,[8] and ketene diethyl acetal[10] were prepared according to literature methods. 2-(Vinylthio)ethyl acetate was prepared by acetylation of the alcohol, which was obtained from Rohm and Haas Co. Ethyl ethynyl ether was obtained from Pfister Chemical Works, and 1-buten-3-ynyl methyl ether was obtained from Chemische Werke Hüls.

3-Ethoxy-*N*-(trichloroacetyl)acrylamide (4a).—Trichloroacetyl isocyanate (9.4 g, 0.05 mol) was added to a stirred solution of 4.0 g (0.056 mol) of ethyl vinyl ether in 25 ml of benzene under a nitrogen atmosphere. The temperature of the mixture was controlled under 50° by an ice bath. The solid that precipitated on standing was removed by filtration. Recrystallization from hexane yielded 10 g (77%) of **4a**: mp 80–82°; ir (Nujol) 5.77, 5.98, and 6.30 μ; nmr (CCl_4) δ 1.43 (t, 3), 4.12 (q, 2), 6.58 (d, 1), 7.95 (d, 1), and 9.67 (s, 1).

Anal. Calcd for $C_7H_8Cl_3NO_3$: C, 32.3; H, 3.1; N, 5.4; Cl, 40.8. Found: C, 32.3; H, 3.3; N, 5.2; Cl, 41.4.

Monitoring Intermediate Formation by Nmr and Ir.—The standard procedure used for detecting cyclic intermediates was as follows. An nmr tube containing *ca.* 150 μl of unsaturated ether in *ca.* 1 ml of CCl_4 with tetramethylsilane as an internal standard was scanned; *ca.* 300 μl of trichloroacetyl isocyanate was added at ambient temperature; and the spectrum again was scanned. Repeated scans were made at appropriate intervals, and the ir spectrum of the solution was recorded when sufficient change was observed in the nuclear magnetic resonance. The procedure was then repeated with CH_3CN as solvent. For **1a** and **1g** in $CDCl_3$, the isocyanate was added to the solution at −45°; however, no additional intermediates were detected at this lower temperature. The pertinent spectral data are given in Table II.

***N*-(3-Ethoxyacryloyl)benzamide.**—A solution of 20 g (0.136 mol) of benzoyl isocyanate and 10 g (0.138 mol) of ethyl vinyl ether in 75 ml of benzene was refluxed under an atmosphere of nitrogen for 8 hr. The white crystals which deposited on cooling were removed by filtration to give 17 g (57%) of crude product. Recrystallization from ethyl alcohol gave 13 g of *N*-(3-ethoxyacryloyl)benzamide: mp 136–138°; ir (KBr) 5.89, 6.05, and 6.32 μ; nmr (CH_2Cl_2) δ 1.37 (t, 3), 4.10 (q, 2), 6.78 (d, 1), 7.80 (m, aromatic protons and C=CHO, 6), and 9.40 (s, 1).

Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.8; H, 5.9; N, 6.4. Found: C, 65.9; H, 5.8; N, 6.4.

3,4-Dihydro-*N*-(trichloroacetyl)-2*H*-pyran-5-carboxamide (4b).—Trichloroacetyl isocyanate (5.7 g, 0.03 mol) was added to a stirred solution of 2.6 g (0.031 mol) of dihydropyran in 10 ml of benzene. When the reaction had been stirred at room temperature for several hours, 30 ml of hexane was added, and the resulting crystals of **4b** were removed by filtration. After the crystals had been washed with ether and dried, the yield was 6.0 g (74%) of **4b**, mp 135–138°. A sample, after recrystallization from ethyl acetate, melted at 136.5–138°: ir (KBr) 5.73, 6.00, and 6.19 μ; nmr ($CDCl_3$) δ 2.00 (m, 2), 2.41 (t, 2), 4.21 (t, 2), 7.75 (s, 1), and 8.85 (broad singlet, 1).

Anal. Calcd for $C_8H_8Cl_3NO_3$: C, 35.3; H, 3.0; N, 5.1; Cl, 39.0. Found: C, 34.9; H, 3.1; N, 5.1; Cl, 39.0.

4-Ethoxy-3,3-dimethyl-1-(trichloroacetyl)-2-azetidinone (2c) and 6-Ethoxy-5,6-dihydro-5,5-dimethyl-2-(trichloromethyl)-4*H*-1,3-oxazin-4-one (3c).—Two runs were made using different solvents, CCl_4 and CH_3CN. Trichloroacetyl isocyanate (1.0 g, 0.01 mol) was added with stirring to 1.75 g (0.01 mol) of ethyl 2-methylpropenyl ether (**1c**) in 5 ml of solvent. After the mixture had been stirred 30 min at room temperature, the ir spectra indicated that the reaction in CH_3CN was complete and that the reaction in CCl_4 was about one-half complete. The CCl_4 mixture was stirred for an additional 3.5 hr. The solvents were removed by rotary evaporation to give a mixture of **2c** and **3c** in the ratio of 3:2. The yield of the mixture was 2.3 g (80%) from CCl_4 and 2.5 g (87%) from CH_3CN. These neat mixtures after standing for several days changed to a ratio of 2:3. The elemental analysis was done on the latter mixture.

Anal. Calcd for $C_9H_{12}Cl_3NO_3$: C, 37.5; H, 4.2; Cl, 36.9; N, 4.9. Found: C, 37.3; H, 4.2; Cl, 37.0; N, 4.8.

2-{[3-Oxo-3-(trichloroacetamido)propenyl]thio}ethyl Acetate (6).—Trichloroacetyl isocyanate (5.7 g, 0.03 mol) was added to a stirred solution of 4.5 g (0.03 mol) of 2-(vinylthio)ethyl ace-

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[6] A similar zwitterion was postulated by Lattrell in ref 4.

[7] In addition to postulating a similar interconversion *via* a zwitterion for arylsulfonyl isocyanate cycloadditions, Effenberger proposed a synchronous $\pi 2_s + \pi 2_a$ cycloaddition [F. Effenberger, *Angew. Chem., Int. Ed. Engl.*, **8**, 295 (1969)]; see ref 2 also.

[8] (a) A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **27**, 3742 (1962); (b) *ibid.*, **28**, 1805 (1963).

[9] Speziale and Smith reported a boiling point of 80–85° (20 mm); on repeated preparations we observed that the material distilled at 58° (30 mm).

[10] "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 506.

TABLE II

SPECTRAL DATA FOR UNSATURATED ETHERS AND CYCLIC INTERMEDIATES

1a	Nmr (CCl_4) δ 1.28 (t, 3, J = 7.0 Hz), 3.68 (q, 2, J = 7.0 Hz), 3.86 (d of d, 1, J = 7.0 and 2.0 Hz), 4.03 (d of d, 1, J = 14.0 and 2.0 Hz), and 6.32 (d of d, 1, J = 7.0 and 14.0 Hz)
3a	Nmr (CCl_4) δ 1.28 (t, 3, J = 7.0 Hz), 2.70 (d of d, 1, J = 2.5 and 15.5 Hz), 3.08 (d of d, 1, J = 4.0 and 15.5 Hz), 3.90 (m, 2, J = 7.0 Hz), and 5.92 (d of d, 1, J = 4.0 and 2.5 Hz); ir (neat) 5.66 and 6.15 μ
1b	Nmr (CCl_4) δ 1.80–2.10 (complex, 4), 3.85 (t of d, 2, J = 5.0 and 1.5 Hz), 4.50 (complex, 1), and 6.20 (d of t, 1, J = 6.5 and 1.5 Hz)
2b	Nmr (CCl_4) δ 1.50–2.15 (complex, 4), 3.55 (complex, 1), 3.70–4.05 (complex, 2), and 5.79 (d, 1, J = 5.5 Hz); ir (CCl_4) 5.48 and 5.90 μ
3b	Nmr (CCl_4) δ 1.50–2.15 (complex, 4), 3.92 (m, 1, J = 2.5 Hz), 3.70–4.05 (complex, 2), and 5.92 (d, 1, J = 3.5 Hz); ir (CCl_4) 5.73 and 6.20 μ
1c	Nmr (CCl_4) δ 1.20 (t, 3, J = 7.0 Hz), 1.52 (t, 6, J = 1.0 Hz), 3.61 (q, 2, J = 4.0 Hz), and 5.66 (m, 1, J = 1.5 Hz)
2c	Nmr (CCl_4) δ 1.15–1.40 (complex, 9), 3.50–4.25 (complex, 2), and 5.21 (s, 1); ir (neat) 5.50 and 5.83 μ
3c	Nmr (CCl_4) δ 1.15–1.40 (complex, 9), 3.50–4.25 (complex, 2), and 6.03 (s, 1); ir (neat) 5.75 and 6.20 μ
1d	Nmr (CCl_4) δ 1.22 (t, 3, J = 6.5 Hz), 1.50 (d of d, 3, J = 7.0 and 1.5 Hz), 3.70 (q, 2, J = 7.0 Hz), 4.23 (d of d, 1, J = 13.0 and 6.5 Hz), and 5.80 (d of m, 1, J = 6.5 and 1.5 Hz)
2d	Nmr (CCl_4) δ 1.20 (d, 3, J = 7.0 Hz), 1.25 (t, 3, J = 7.0 Hz), 2.90 (d of d, 1, J = 7.0 and 5.5 Hz), 3.95 (q, 2, J = 7.0 Hz), and 5.52 (d, 1, J = 5.5 Hz); ir (CCl_4) 5.52 and 5.80 μ
3d	Nmr (CCl_4) δ 1.20 (d, 3, H = 7.0 Hz), 1.25 (t, 3, J = 7.0 Hz), 3.03 (d of d, 1, J = 7.0 and 4.0 Hz), 3.90 (q, 2, J = 7.0 Hz), and 5.75 (d, 1, J = 4.0 Hz); ir (CCl_4) 5.70 and 6.15 μ
1e	Nmr (CCl_4) δ 1.21 (t, 3, J = 7.0 Hz), 1.50 (d of d, 3, J = 6.5 and 1.5 Hz), 3.60 (q, 2, J = 7.0 Hz), 4.59 (d of q, 1, J = 12.5 and 6.5 Hz), and 6.10 (d, 1, J = 12.0 and 1.5 Hz)
2e	Nmr (CCl_4) δ 1.20 (d, 3, J = 7.0 Hz), 1.28 (t, 3, J = 7.0 Hz), 3.1 (complex, 1), 3.85 (q, 2, J = 7.0 and 5.0 Hz), and 5.11 (d, 1, J = 2.0 Hz); ir (CCl_4) 5.50 and 5.80 μ
3e	Nmr (CCl_4) δ 1.20 (d, 3, J = 7.0 Hz), 1.25 (t, 3, J = 7.0 Hz), 3.05 (d of d, 1, J = 7.0 and 5.0 Hz), 3.90 (q, 2, J = 7.0 Hz), and 5.46 (d, 1, J = 5.0 Hz); ir (CCl_4) 5.70 and 6.15 μ
1g	Nmr (CCl_4) δ 1.26 (t, 3, J = 7.0 Hz), 2.94 (s, 1), and 3.73 (q, 2, J = 7.0 Hz)

tate in 30 ml of benzene under an atmosphere of nitrogen. The reaction was not noticeably exothermic. After the reaction mixture had been stirred for 10 hr at room temperature, the solvent was removed *in vacuo* to give 6 g (60%) of crude **6**, mp 110–113°. Two recrystallizations from ethyl acetate afforded 3.0 g of **6**: mp 114.5–116.5°; ir (KBr) 5.75 and 6.03 μ; nmr (CH_2Cl_2) δ 2.06 (s, 3), 3.08 (t, 2), 4.31 (t, 2), 7.06 (d, 1), 7.59 (d, 1), and 9.08 (broad singlet, 1).

Anal. Calcd for $C_9H_{10}Cl_3NO_4S$: C, 32.3; H, 3.0; N, 4.2; Cl, 31.8; S, 9.6. Found: C, 32.6; H, 3.1; N, 3.9; Cl, 32.3; S, 9.6.

6,6-Dimethoxy-5,5-dimethyl-2-(trichloromethyl)-4*H*-1,3-oxazin-4-one (3f).—Trichloroacetyl isocyanate (5.7 g, 0.03 mol) was added to a stirred solution of 3.6 g (0.031 mol) of dimethylketene dimethyl acetal (**1f**) in 25 ml of benzene under an atmosphere of nitrogen. The reaction temperature gradually climbed to 40° before receding. The solvent was removed *in vacuo* and the residue crystallized to give **3f** in a quantitative yield. The product was extremely hygroscopic. A small sample, recrystallized twice from hexane, melted at 53–54°: nmr (CCl_4) δ 1.50 (s, 6), 3.37 (s, 3), and 3.75 (s, 3).

3,3-Diethoxy-*N*-(trichloroacetyl)acrylamide (4g).—Trichloroacetyl isocyanate (5.7 g, 0.03 mol) was added to a stirred solution of 3.6 g (0.03 mol) of ketene diethyl acetal (**1g**) in 25 ml of benzene under a nitrogen atmosphere. The temperature of the mixture was controlled under 50° by an ice bath. A solid which precipitated was removed by filtration, recrystallized from ethyl acetate, and washed with ether to give 3.7 g (40%) of **4g**: mp 140–143°; ir (KBr) 5.72, 6.00, and 6.26 μ; nmr ($CHCl_3$) δ 1.44 (t, 6), 4.16 (q, 2), 4.45 (q, 2), 4.80 (s, 1), and 10.1 (broad singlet, 1).

Anal. Calcd for $C_9H_{12}Cl_3NO_4$: C, 35.5; H, 4.0; N, 4.6; Cl, 34.9. Found: C, 35.9; H, 4.0; N, 4.4; Cl, 34.9.

6-Ethoxy-2-(trichloromethyl)-4*H*-1,3-oxazin-4-one (7a).—A 5.0-g (0.027 mol) portion of trichloroacetyl isocyanate was added with stirring and cooling to 2.1 g (0.030 mol) of ethyl ethynyl ether in 15 ml of carbon tetrachloride under nitrogen. After 30 min at room temperature, the solvent was removed by rotary evaporation at reduced pressure to give 7.0 g (100%) of **7a**: mp 61–64°; ir (Nujol) 6.05 and 6.24 μ; nmr (CCl_4) δ 1.53 (t, 3, J = 7.0 Hz), 4.38 (q, 2, J = 7.0 Hz), and 5.50 (s, 1).

Anal. Calcd for $C_7H_6Cl_3NO_3$: C, 32.4; H, 2.3; N, 5.2. Found: C, 31.9; H, 2.7; N, 5.1.

6-Ethoxy-2-phenyl-4*H*-1,3-oxazin-4-one (7b).—Benzoyl isocyanate (20 g, 0.136 mol) was added to a stirred solution of 10 g (0.143 mol) of ethyl ethynyl ether (**1a**) in 100 ml of benzene under a nitrogen atmosphere. The temperature of the mixture was controlled between 30 and 40° with an ice bath. As the solution cooled, a finely divided solid precipitated. This solid was removed by filtration, washed thoroughly with hexane, and dried in a vacuum oven to give 25 g (85%) of **7b**, mp 132–135°. Recrystallization from a mixture of benzene and hexane yielded 22 g of **7b**: mp 133.5–135° dec; ir (KBr) 6.11, 6.31, and 6.40 μ; nmr (acetone) δ 0.65 (t, 3), 3.80 (q, 2), 4.75 (s, 1), and 7.20 (m, 5).

Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.4; H, 5.1; N, 6.4. Found: C ,66.4; H, 5.1; N, 6.3.

Ethyl *N*-(Trichloroacetyl)malonamate (8a) by Hydrolysis of 7a.—A sample of **7a** was placed in a nmr tube containing acetonitrile. When an excess of moist formic acid was added, the disappearance of **7a** and the appearance of **8a** were observed by nmr. The reaction required about 2 hr at room temperature. Although the product was not isolated, its ir and nmr spectra were recorded: ir (Nujol) 3.15, 5.65, 5.78, and 5.83 μ; nmr (CH_3CN, HCOOH) δ 1.30 (t, 3, J = 7.0 Hz), 3.80 (s, 2), and 4.40 (q, 2, J = 7.0 Hz) (NH obscured by formic acid).

Ethyl *N*-Benzoylmalonamate (8b) by Hydrolysis of 7b.—A suspension of 5 g of **7b** in 80 ml of water containing 10 ml of 10% HCl was stirred for 15 min at room temperature. The solid was removed by filtration, washed with water, and dried in an oven at 80° to give 5.7 g of crude **8b**, melting at 102–110°. Recrystallization from a mixture of benzene and hexane yielded 5.4 g of **8b**, mp 114.5–115.5° (lit.[11] mp 114.5–115.5°).

Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.3; H, 5.6; N, 6.0. Found: C, 61.5; H, 5.8; N, 6.0.

Ethyl *N*-Benzylmalonamate (9) by Hydrogenation of 8b.—A solution of 5 g of **8b** in 200 ml of ethyl acetate was hydrogenated at room temperature and 40 psi over 3 g of 5% palladium on carbon. After hydrogen absorption ceased, the catalyst was removed by filtration and the filtrate evaporated to yield 4.2 g of **9**: mp 46–49°; ir (KBr) 5.81 and 6.08 μ; nmr (CCl_4) δ 1.10 (t, 3), 3.08 (s, 2), 3.95 (q, 2), 4.19 (d, 2), 7.12 (s, 5), and 8.06 (broad singlet, 1).

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.1; H, 6.8; N, 6.3. Found: C, 65.4; H, 6.7; N, 6.4.

6-(2-Methoxyvinyl)-2-(trichloromethyl)-4*H*-1,3-oxazin-4-one (10).—A solution of 2.6 g (0.032 mol) of 1-buten-3-ynyl methyl ether and 5.7 g (0.03 mol) of trichloroacetyl isocyanate in 25 ml of benzene was stirred for several days at room temperature under nitrogen. The crystals that precipitated were filtered and dried to give 6.0 g of **10**. A sample for analysis was recrystallized twice from ethyl acetate and dried in a vacuum desiccator to give a product with mp 126–127.5°; ir (KBr) 5.95, 6.08, and 6.20 μ; nmr (CH_3CN) δ 3.80 (s, 3), 5.69 (d, 1), 5.94 (s, 1), and 7.57 (d, 1).

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Anal. Calcd for $C_8H_6Cl_3NO_3$: C, 35.5; H, 2.2; N, 5.2; Cl, 39.3. Found: C, 35.7; H, 2.3; N, 5.5; Cl, 39.4.

Registry No.—**1a**, 109-92-2; **1b**, 110-87-2; **1c**, 927-61-7; **1d**, 4696-25-7; **1e**, 4696-26-8; **1g**, 2678-54-8; **2b**, 29669-00-9; **2c**, 29669-01-0; **2d**, 29669-02-1; **2e**, 29669-03-2; **3a**, 29669-04-3; **3b**, 29669-05-4; **3c**, 29784-75-6; **3d**, 29669-06-5; **3e**, 29669-07-6; **3f**, 29669-08-7; **4a**, 29669-09-8; **4b**, 29784-76-7; **4g**, 29669-10-1; **6**, 29669-11-2; **7a**, 29669-12-3; **7b**, 29669-13-4; **8a**, 29784-77-8; **9**, 29689-63-2; **10**, 29689-64-3; trichloroacetyl isocyanate, 3019-71-4; *N*-(3-ethoxyacryloyl)benzamide, 29689-66-5.

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Synthesis of 3-Alkoxyoxetanes

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3-Alkoxyoxetanes are prepared by chlorination of allyl alcohol in the presence of an excess of an aliphatic alcohol (including allyl alcohol) followed by ring closure with hot aqueous NaOH. The product distribution during chlorination is consistent with a carbonium ion mechanism, yielding 2,3-dichloropropanol and the isomers 2-alkoxy-3-chloropropanol and 3-alkoxy-2-chloropropanol in the ratio of about 65:35. Side reactions include oxidation and ether formation by reaction of the three main chlorination products with the intermediate carbonium ion. The yield of the three major chlorination products is 65–80%. Yields of alkoxyoxetane based on 2-alkoxy-3-chloropropanol are in the range of 55–75%. A series of alkoxyoxetanes, $\overline{\mathrm{OCH_2CH(OR)CH_2}}$, were prepared where R = methyl, ethyl, allyl, *n*-butyl, cyclohexyl, and *n*-dodecyl. These were treated with anhydrous HCl to form the pure precursor 2-alkoxy-3-chloropropanol.

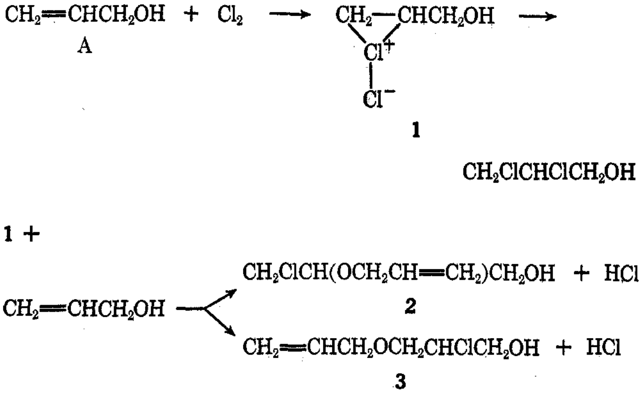
The halogenation of olefins in reactive (nucleophilic) solvents has been studied extensively. The reaction proceeds *via* a carbonium ion mechanism involving intermediate halonium ions. In alcoholic media, the main products are ethers and dihalides.[2–4]

We have studied the chlorination of allyl alcohol since the dichloropropanol and 1,2- and 1,3-chlorohydrin ethers produced offer a route to alkoxyoxetanes as well as epichlorohydrin and alkyl glycidyl ethers.

The present work deals with the synthesis of a series of 3-alkoxyoxetanes[5] and their reaction with anhydrous hydrogen chloride to produce pure 2-alkoxy-3-chloropropanols.

Discussion

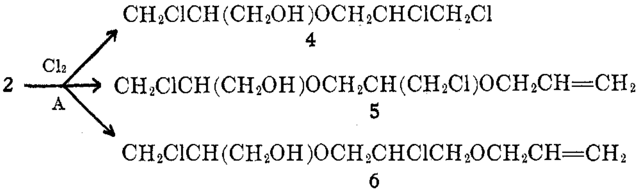
Chlorination of allyl alcohol in the absence of water leads mainly to chlorohydrin ethers, dichloropropanol, and oxidation products. Dichloropropanol formation is initially competitive with ether formation; the respective rates of formation remain approximately the same over the first 20% reaction. At higher conversion, it is expected that dichloropropanol formation would increase relative to ether formation due to the increased HCl concentration (**1** + Cl⁻ → $CH_2ClCHClCH_2OH$). The isomeric allyloxychloropropanols (**2** and **3**) are formed in the ratio of about 65:35.



$$CH_2{=}CHCH_2OH + Cl_2 \longrightarrow CH_2{=}CHCHO + 2HCl$$

The initial oxidation product is probably acrolein but it rapidly undergoes further reaction producing an acetal containing a labile chlorine. Acrolein can add HCl and form acetals of β-chloropropionaldehyde.[6] Chlorination followed by acetal formation would give $CH_2ClCHClCH(OR)_2$, $CH_2{=}CHCH_2OCH_2CHClCH(OR)_2$, and $CH_2ClCH(OCH_2CH{=}CH_2)CH(OR)_2$.

The conversion of allyl alcohol was kept low (about 20%) to minimize formation of polyethers resulting from chlorination of the allyloxychloropropanols. A similar reaction can be written for the linear ether **3**. The same products can be formed by reaction of the intermediate carbonium ion **1** with 2,3-dichloropropanol and with **2** and **3**.



Hennion[7] reported the preparation of 2-allyloxy-3-chloropropanol (but not the linear isomer) in 36% yield by reaction of *tert*-butyl hypochlorite with allyl alcohol but did not study its reaction with base. Later work has shown that reaction of *tert*-BuOCl with allyl alcohol

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