(21) In comparing rates of reactions having different kinetic orders, one must consider the concentrations

$$\frac{v_{\text{hexane}}}{v_{\text{THF}}} = \frac{k_{\text{hexane}}}{k_{\text{THF}}}\frac{(0.138)^{1/3}}{(0.561)} = \frac{1.53 \times 10^{-3}}{7.7 \times 10^{-7}}\frac{(0.517)}{(0.561)} \simeq 2 \times 10^{3}$$

Likewise, for comparing the initial $v_{0\%}$ with $v_{50\%}$ (eq 8), one notes that

$$\frac{v_{0\%}}{v_{50\%}} = \frac{k_{0\%}}{k_{50\%}}\frac{(0.259)^{1/3}}{(0.259)^{1/2}} = \frac{3.52 \times 10^{-4}}{3.45 \times 10^{-5}}\frac{(0.637)}{(0.502)} \simeq 13$$

(22) S. S. Kuo, "Numerical Methods and Computers," Addison-Wesley, Reading, Mass., 1965, p 225.

(23) J. N. Hay, G. R. Jones, and J. C. Robb, *J. Organometal. Chem.*, **15**, 295 (1968).

(24) G. M. Clark and G. Zweifel, *J. Amer. Chem. Soc.*, **93**, 527 (1971).

(25) Hay, *et al.*,[23] observed half-order dependence on **2** in the reaction of **2** with 1-butene. They interpreted their kinetic order in terms of dissociation of hydride trimer to dimer and monomer, followed by slow addition of monomer to the olefin. They neglect to account for the kinetic role of the dimer. The observed one-half order can be reconciled with their mechanism only by making special assumptions: that [monomer] = [dimer] and that $k_{\text{monomer}} = 2k_{\text{dimer}}$. The first assumption is valid only at the early stage of the reaction, and the latter would just be fortuitous; *cf.* case Ia and S. G. Rhee, Doctoral Dissertation, The Catholic University of America, Washington, D.C., 1972, pp 124–129. A better explanation of Hay's results is that the hydride used contained 5–10% of triisobutylaluminum, which could form mixed complexes with **2**, $R'_3Al \cdot nR'_2AlH$,[26,27] which would increase the kinetic order of the hydride source because of the lower reactivity of such complexes.

(26) J. J. Eisch and S. G. Rhee, *J. Organometal. Chem.*, **31**, C49 (1971).

(27) E. G. Hoffmann and G. Schomburg, *Z. Elektrochem.*, **61**, 1101, 1100 (1957).

(28) K. W. Egger, *J. Amer. Chem. Soc.*, **91**, 2867 (1969).

(29) The ΔH for both $(R'_2AlH)_3$ and $(R'_2AlD)_3$ are unknown, but it is known that the heats of vaporization for H_2O and D_2O are 9.717 and 9.927 kcal/mol, respectively: D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford University Press, London, 1969, p 100.

(30) P. R. Jones, *J. Org. Chem.*, **37**, 1886 (1972).

(31) J. J. Eisch and S. G. Rhee, unpublished studies.

(32) J. J. Eisch and R. Amtmann, *J. Org. Chem.*, **37**, 3410 (1972).

(33) J. J. Eisch and C. K. Hordis, *J. Amer. Chem. Soc.*, **93**, 2974 (1971).

(34) J. J. Eisch and W. C. Kaska, *J. Org. Chem.*, **27**, 3745 (1962).

(35) E. Bonitz, *Chem. Ber.*, **88**, 742 (1955).

(36) D. F. Hagen and W. D. Leslie, *Anal. Chem.*, **35**, 814 (1963).

(37) J. H. Mitchen, *Anal. Chem.*, **33**, 1331 (1961).

(38) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, p 203.

(39) The loss of diisobutylaluminum hydride from 13c could give rise also to *cis*- and *trans*-3-octenes. Since the analytical methods could not distinguish between these position isomers, all the octenes were considered as "4-octenes."

(40) S. G. Rhee, Doctoral Dissertation, The Catholic University of America, Washington, D.C., 1972.

Reaction of *N,N*-Dichlorourethane and of Diethyl Azodicarboxylate with Alkoxide[1]

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Abstract: Exposure of *N,N*-dichlorourethane (**1**) to sodium methoxide gave high yields of ethyl methyl carbonate (**2**) and nitrogen gas. Several mechanistic possibilities were considered, including (A) generation of chloronitrene (**4**) *via* NCl_2^-, (B) attack of base on the chlorine site, and (C) formation of an *N*-chloro nitrogen radical. Diethyl azodicarboxylate (**14**), a proposed intermediate in both (B) and (C), was rapidly decomposed by ethoxide to diethyl carbonate, nitrogen, and diethyl hydrazine-1,2-dicarboxylate. Possibility B was eliminated since treatment of **1** with potassium monochlorourethane did not yield **14**. A labeling experiment involving **1**-^{15}N and isopropyl *N,N*-difluorocarbamate yielded $^{15}N{\equiv}N$, in accord with (A) but not with (C).

N-Chlorocarbamates are versatile reagents which can react with a variety of substrates by either radical or polar pathways.

Good yields of adducts were obtained from *N,N*-dichlorourethane (DCU) and unsaturated substrates, such as styrene.[4,5] A similar, facile reaction occurred with conjugated dienes.[6] In a number of cases, a metal ion redox system was employed, as in the addition of *N*-monochlorocarbamates to cyclohexene.[7] Uv light has also been used as the initiator.[8] For these examples, evidence pointed to the involvement of radical intermediates. In the presence of aluminum chloride, apparently DCU, styrene, and acetonitrile participate in ionic processes leading to an imidazoline product.[9]

Various transformations entail halogenation. For example, *N*-monochlorourethane (MCU) converted benzylamine to the *N*-mono- or *N,N*-dichloro derivative.[10] Exposure of ethyl ether to DCU resulted in chlorination and scission of the ether, presumably *via* a homolytic mechanism.[11] An intriguing result, involving formation of 3,3,5-trichlorooxindole, was observed on interaction of DCU and indole-2-carboxylic acid.[12,13]

With triphenylphosphine, replacement of the halogen in DCU gave rise to ethyl triphenylphosphazocarboxylate.[14] A similar pathway was followed with the sodium salt of MCU.[14] The amide proton of MCU is fairly acidic, giving rise to salts on exposure to strong base.[15,16]

The principal aim of our work was to determine the response of DCU to alkoxide ion. Of interest was the nature of the reaction pathway, particularly in relation to the possible generation of dichloroamide ion and chloronitrene. In connection with this study, the behavior of diethyl azodicarboxylate toward alkoxide was also examined.

Results and Discussion

N,N-Dichlorocarbamates have been prepared by passing chlorine into a solution of the carbamate in buffered acetic acid.[5] Our procedure for *N,N*-dichlorourethane (DCU, **1**) entailed treatment of the carbamate with calcium hypochlorite in hydrochloric acid. A reverse disproportionation reaction was employed for the synthesis of *N*-monochlorourethane (MCU) from DCU and urethane.[17] The anhydrous potassium salt of MCU was obtained by exposure to 1 equiv of potassium hydroxide in methanol.[16]

In the presence of 1.5 equiv of sodium methoxide in methanol at 0°, DCU decomposed rapidly and cleanly to ethyl methyl carbonate (**2**), nitrogen, and sodium chloride (eq 1).

Identification of the ester was accomplished by compari-

$$\underset{1}{2\mathrm{EtO_2CNCl_2}} + 3\mathrm{NaOMe} \longrightarrow \underset{2}{2\mathrm{EtO_2COMe}} + \mathrm{N_2} + 3\mathrm{NaCl} + \mathrm{MeOCl} \quad (1)$$

son of the glpc retention time and the ir and nmr spectra with those of authentic material prepared by reaction of ethyl chloroformate with sodium methoxide. The identity of nitrogen was established by gas chromatography on molecular sieves.

The indicated stoichiometry is borne out by the data in Table I. High yields of both ethyl methyl carbonate and nitrogen gas were observed. In one run, excess alkoxide was used, but no significant change in yields resulted as compared with the case involving the stoichiometric quantity of sodium methoxide. In one experiment, the amount of positive chlorine present at the end of reaction, determined by iodometry, was 26% of the original, in good agreement with the value (25%) predicted by eq 1. Methyl formate, a minor side product, appears to arise from oxidation[18] of solvent methanol, first to formaldehyde, and then to formic acid which is then esterified. In a control experiment to determine the sensitivity of methanol to oxidation, it was observed that methanol was oxidized to the extent of 2-5% (based on positive chlorine) by DCU or sodium hypochlorite under conditions similar to the standard procedure. This figure is in the same range as the yield of methyl formate. Other alcohols, such as ethanol and 2-propanol, were very quickly oxidized by DCU.

Table I. *N*,*N*-Dichlorourethane and Sodium Methoxide

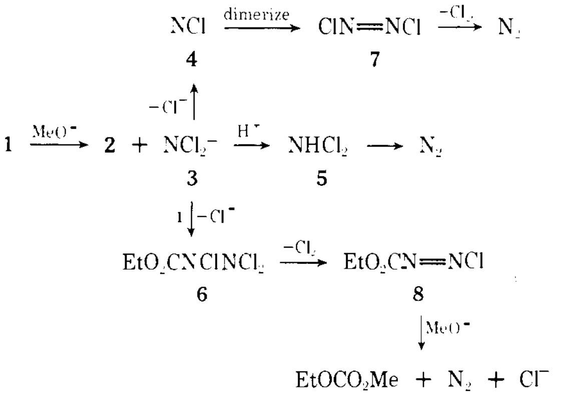
Products, % yield				
$\mathrm{EtOCO_2Me}$	$\mathrm{N_2}$[a]	NaCl[b]	Positive Cl[c]	Other
92[d]	104	64	*e*	6[f]
93[g]	93	81	26	7[h]

[a] Assuming all gas evolved is nitrogen. [b] % yield based on sodium. [c] % of original. [d] 25 mmol of NaOMe. [e] Not determined. [f] $\mathrm{HCO_2Me}$, 6%. [g] Stoichiometric amount of NaOMe (18.7 mmol). [h] $\mathrm{HCO_2Me}$, 5%; 2% unidentified.

Reaction Mechanism. Several pathways will be considered as possibilities in the reaction with strong base. The three which seem most likely involve (A) attack of base on carbonyl, (B) attack of base on chlorine, and (C) formation of an *N*-chloro nitrogen radical.

A. Inspection of eq 1 suggests attack at carbonyl with displacement of dichloroamide ion (**3**). This approach is diagrammed in detail in Scheme I. Dichloroamide ion might expel chloride ion by α-elimination forming chloronitrene (**4**), abstract a proton from solvent to give dichloramine (**5**), or attack a second molecule of **1** yielding the trichlorohydrazide (**6**). Through dimerization, chloronitrene would be expected to produce dichlorodiazene (**7**) which serves as precursor to nitrogen. Dichloramine (**5**) is known to decompose to nitrogen in basic solution,[19] probably by reversion to **3**. Finally, if **6** were formed, loss of chlorine would produce the chloro azo compound **8** which would conceivably react with methoxide to give the ester, nitrogen, and chloride ion.

Scheme I



The individual steps will be considered in greater detail. The initial one, attack at carbonyl, has literature analogy. Klopotek and Hobrock observed[20] this mode of reaction in a very similar system, isopropyl *N*,*N*-difluorocarbamate and potassium *tert*-butoxide (eq 2). The leaving group, difluoroamide ion, then decomposed by loss of fluoride ion to fluoronitrene. Very good evidence for the intermediacy of fluoronitrene was provided by isolation of its dimer, difluorodiazene. In addition, fluoronitrene combined with primary amines, yielding adducts which underwent loss of nitrogen to give good yields of the corresponding hydrocarbons[20a] (eq 3).

$$i\text{-}\mathrm{PrO_2CNF_2} + t\text{-}\mathrm{BuO} \longrightarrow i\text{-}\mathrm{PrOCO_2}\text{-}t\text{-}\mathrm{Bu} + \mathrm{NF_2}^- \xrightarrow{-\mathrm{F}^-} \mathrm{NF} \xrightarrow{\text{dimerize}} \mathrm{FN{=}NF} \quad (2)$$

$$\mathrm{RNH_2} + \mathrm{NF} \longrightarrow \mathrm{R\overset{+}{N}H_2\overset{-}{N}F} \xrightarrow{-\mathrm{HF}} \mathrm{RN{=}NH} \longrightarrow \mathrm{RH} + \mathrm{N_2} \quad (3)$$

Similarly, fluorination of urethanes in aqueous solution formed difluoramine,[21] presumably *via* the route indicated in eq 4.

$$\mathrm{RO_2CNH_2} \xrightarrow{\mathrm{F_2}} \mathrm{RO_2CNF_2} \xrightarrow[\substack{-\mathrm{ROH}\\ -\mathrm{CO_2}}]{\mathrm{H_2O}} \mathrm{NF_2}^- \xrightarrow{\mathrm{H}^+} \mathrm{HNF_2} \quad (4)$$

N-Monofluorourethane combined with aqueous sodium hypochlorite to yield dichlorofluoroamine, most likely by way of chlorofluoroamide ion[21] (eq 5).

$$\mathrm{EtO_2CNHF} \xrightarrow{\mathrm{OCl}^-} \mathrm{EtO_2CNClF} \xrightarrow[\substack{-\mathrm{EtOH}\\ -\mathrm{CO_2}}]{\mathrm{HO}^-} \mathrm{NClF}^- \xrightarrow{+\mathrm{Cl}^+} \mathrm{NFCl_2} \quad (5)$$

Since dichloroamide ion may be considered a pseudo halide, compounds such as DCU then are pseudo acyl halides. The conjugate acid of dichloroamide ion is dichloramine (**5**). Estimation of the acid dissociation constant of **5** gives a $\mathrm{p}K_\mathrm{a}$ value[22] of 7 ± 3. Evidently **5** is considerably more acidic than methanol ($\mathrm{p}K_\mathrm{a} = 16$) or water ($\mathrm{p}K_\mathrm{a} = 15.7$). In fact, solutions of **5** in the pH range 5–8 should contain an appreciable concentration of dichloroamide ion.[22] Hence, it is not likely that $\mathrm{NCl_2}^-$ would be protonated to $\mathrm{HNCl_2}$ to any large extent in our case. In view of the low $\mathrm{p}K_\mathrm{a}$ of **5**, one would expect $\mathrm{NCl_2}^-$ to be a reasonably good leaving group. For comparison, acetic acid has $\mathrm{p}K_\mathrm{a} = 5$, and acetate is recognized as a good leaving group.

Once $\mathrm{NCl_2}^-$ is liberated, it may expel a chloride ion, giving chloronitrene (**4**), a process which has literature analogy. In addition to the well-established formation of dichlorocarbene from trichloromethyl anion, one may cite the decomposition of difluoroamide ion to fluoronitrene in both the *N*,*N*-difluorourea[23] and isopropyl *N*,*N*-difluorocarbamate[20] systems.

Chloronitrene, on the other hand, is not a well-established entity.[24] Although its reactions should generally parallel those of fluoronitrene, there may be a greater tendency to react in other ways, *e.g.*, hydrogen abstraction which would generate monochloramine, a precursor of nitrogen under basic conditions.[19] Chloronitrene could conceivably attack a molecule of starting *N*,*N*-dichloroamide (eq 6). The intermediate adduct (**9**) would most likely give rise to the chloroacyldiazene (**11**) which presumably reacts easily with methoxide, generating the ester, nitrogen, and chloride ion.

$$\mathrm{EtO_2CNCl_2} + \mathrm{NCl} \longrightarrow \underset{\mathbf{9}}{\mathrm{EtO_2C\overset{+}{N}Cl_2\overset{-}{N}Cl}} \longrightarrow$$

$$\underset{\mathbf{10}}{\mathrm{EtO_2CNClNCl_2}} \xrightarrow{-\mathrm{Cl_2}} \underset{\mathbf{11}}{\mathrm{EtO_2CN{=}NCl}} \xrightarrow{\mathrm{MeO^-}}$$

$$\mathrm{EtO_2COMe} + \mathrm{N_2} + \mathrm{Cl^-} \quad (6)$$

One might also expect attack of NCl_2^- on starting material. Replacement of chloride (eq 7) would lead to trichlorohydrazide (**10**) whose expected behavior is illustrated in eq 6. Displacement of halide from *N*-chloroamines by various nucleophiles is documented in the literature;[19] *e.g.*, ammonia reacts with monochloramine to yield hydrazine and ammonium chloride.

$$1 + \mathrm{NCl_2^-} \xrightarrow{-\mathrm{Cl^-}} \underset{\mathbf{10}}{\mathrm{EtO_2CNClNCl_2}} \quad (7)$$

To gain additional information pertinent to the proposal involving NCl_2^- and NCl, an experiment was undertaken with DCU-^{15}N and isopropyl *N,N*-difluorocarbamate (DFC). By including DFC, which is known to generate fluoronitrene,[20] in the reaction between DCU-^{15}N and sodium methoxide, it might be possible to observe mixed dimerization of ^{15}NCl and NF, thus leading theoretically to N_2, $^{15}N{\equiv}N$, and $^{15}N_2$.

$$^{15}\mathrm{NCl} \xrightarrow{\mathrm{NF}} \mathrm{Cl{-}^{15}N{=}NF} \xrightarrow{-\mathrm{ClF}} {}^{15}\mathrm{N{\equiv}N} \quad (8)$$

$$^{15}\mathrm{NCl_2^-} \xrightarrow{\mathrm{NF}} {}^{15}\mathrm{NCl_2{-}\overset{-}{N}F} \xrightarrow{-\mathrm{Cl^-}} \mathrm{Cl{-}^{15}N{=}NF} \xrightarrow{-\mathrm{ClF}} {}^{15}\mathrm{N{\equiv}N} \quad (9)$$

In a control run, the mixture of unlabeled DCU and DFC reacted smoothly with sodium methoxide, giving a mixture of gases and good yields of ethyl methyl (85%) and isopropyl methyl carbonates (86%) with minor amounts of $MeOCO_2Me$ and i-$PrOCO_2$-i-Pr. Mass spectral analysis of the evolved gas is included in Table II.

Reaction of DCU-^{15}N and DFC with sodium methoxide yielded nitrogen (mixture of isotopes, 72% yield), dimethyl carbonate (31%), ethyl methyl carbonate (60%), isopropyl methyl carbonate (>90%), and diisopropyl carbonate (5%). Mass spectral analysis of the off-gas revealed the presence of N_2, $^{15}N{\equiv}N$, and $^{15}N_2$ in the ratio 1:2.0:3.5, accounting for at least 90% of the nitrogen-15. By comparing the runs with unlabeled and labeled DCU, it is evident that no correction is necessary for the intensity of the $^{15}N{\equiv}N$ signal, while *ca.* 20% of the *m/e* 30 peak may be due to NO. Correction for NO does not substantially alter the ratios.

There are three reasonable routes to account for $^{15}N{\equiv}N$: (a) mixed dimerization of ^{15}NCl and NF, (b) reaction[20] of $^{15}NCl_2^-$ with NF, and (c) combination of DCU-^{15}N with NF. Possibilities a and b (eq 8 and 9) are both in accord with attack of methoxide on carbonyl with generation of NCl_2^-. The intermediate product, chlorofluorodiazene, would probably decompose to give nitrogen. The third possibility is somewhat analogous to the reaction of fluoronitrene with primary amines,[20a] eq 3. However, we deem this less likely than (a) or (b). From an estimation of relative basicities, it would appear more reasonable that NF would attack methanol.

Table II. Mass Spectral Data for Gases from DCU and DCU-^{15}N with DFC

m/e	Ion	—Relative intensity, %— DCU	DCU-^{15}N
28	N_2^+	89.2	11.2
29	$^{15}N{\equiv}N^+$	0.3	22.1
30	$^{15}N_2^+$, NO^+	7.8	39.0
44	CO_2^+	1.3	1.4
85	SiF_3^+	1.1	25.1
Other		0.2	1.2

The nitrogen species of *m/e* 28 results from dimerization of NF and that of *m/e* 30 from N–N bond formation involving interaction of moieties derived from DCU-^{15}N. The fact that $^{15}N_2$ is formed to a greater extent than $^{15}N{\equiv}N$ may be a consequence of the faster rate of decomposition of DCU-^{15}N.

Silicon tetrafluoride was identified[25] in both reactions with DFC on the basis of a prominent peak at *m/e* 85. Small amounts of CO_2 and NO were also present. Carbon dioxide was previously observed as an important product from DFC and *tert*-butoxide.[20] Nitric oxide, which has not been mentioned by prior investigators, may be derived from NF and small amounts of residual oxygen. When the DCU-DFC reaction was run under an ordinary atmosphere, large amounts of NO were formed. In contrast to previous related work with DFC,[20] no difluorodiazene was detected in our reactions, which may be a reflection of the difference in conditions.

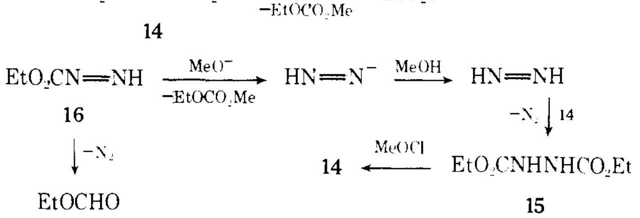
The occurrence of $^{15}N{\equiv}N$ in the collected gas appears to confirm the presence of NCl_2^- and/or NCl in the reaction of DCU with sodium methoxide. On the basis of various observations,[26] a straightforward mechanistic extrapolation from DFC to DCU did not appear justified until the latter stages of our work.

B. In this alternative approach (Scheme II), initial attack of methoxide ion is at a partially positive chlorine atom with displacement[19] of anion **12**. In turn, **12** may attack a second molecule of starting material at nitrogen, displacing chloride and forming a nitrogen-nitrogen bond. Dichlorohydrazide **13** should easily lose chlorine to generate the azo compound **14**. Azo compounds, such as **14** and ^-O_2C-$N{=}NCO_2^-$, are readily decomposed in acidic, basic, or neutral solution, giving nitrogen and the corresponding hydrazine derivative.[27,28] The steps leading from **14** to **15** represent the generally accepted mode of decomposition. Hydrazide **15** would be easily reoxidized[29] to the azo derivative **14** by positive chlorine, as in methyl hypochlorite, and could then be recycled until all nitrogen was in the form of N_2. The overall stoichiometry of Scheme II conforms to that of eq 1.

Because none of the literature examples of azo decomposition involved systems sufficiently close to the present one, a series of experiments was conducted to determine the behavior of diethyl azodicarboxylate (**14**) toward alkoxide. The azo compound decomposed rapidly and nearly quantitatively to diethyl carbonate, diethyl hydrazinedicarboxylate, and nitrogen (eq 10, Table III). Since modest amounts

$$2(\mathbf{14}) + 2\mathrm{EtOH} \xrightarrow{\mathrm{NaOEt}} 2\mathrm{EtO_2COEt} + \mathbf{15} + \mathrm{N_2} \quad (10)$$

Scheme II



$$1 \xrightarrow[-\mathrm{MeOCl}]{\mathrm{MeO^-}} \underset{\mathbf{12}}{\mathrm{EtO_2CNCl^-}} \xrightarrow[-\mathrm{Cl^-}]{1} \underset{\mathbf{13}}{\mathrm{EtO_2CNClNClCO_2Et}} \xrightarrow{-\mathrm{Cl_2}}$$

$$\underset{\mathbf{14}}{\mathrm{EtO_2CN{=}NCO_2Et}} \xrightarrow[-\mathrm{EtOCO_2Me}]{\mathrm{MeO^-}} \mathrm{EtO_2CN{=}N^-} \xrightarrow{\mathrm{MeOH}}$$

$$\begin{tikzcd}
\underset{\mathbf{16}}{\mathrm{EtO_2CN{=}NH}} \arrow[r, "\mathrm{MeO^-}", "-\mathrm{EtOCO_2Me}"'] \arrow[d, "-\mathrm{N_2}"] & \mathrm{HN{=}N^-} \arrow[r, "\mathrm{MeOH}"] & \mathrm{HN{=}NH} \arrow[d, "-\mathrm{N_2}"', "14"] \\
\mathrm{EtOCHO} & \mathbf{14} & \underset{\mathbf{15}}{\mathrm{EtO_2CNHNHCO_2Et}} \arrow[l, "\mathrm{MeOCl}"']
\end{tikzcd}$$

Table III. Diethyl Azodicarboxylate and Sodium Ethoxide

	Products, % yield[a]			
NaOR	$EtOCO_2R$	(Et-OCO-NH)$_2$	N_2	Other
NaOEt[b]	79		140	15[c]
NaOEt[d]	87	86	122	14[e]
NaOEt[f]	87	60	112	7[g]
NaOCl[h,i]	21[j,k]		87[k]	37[k,l]

[a] Based on the stoichiometry of eq 10. [b] 2.2 mmol of NaOEt. [c] HCO_2Et, 15%; 2% unidentified. [d] 5.7 mmol of NaOEt. [e] HCO_2Et, 14%; 18% unidentified. [f] 5.7 mmol of NaOEt; N_2 atmosphere. [g] HCO_2Et, 4%; CO_2, 3%. [h] 5% NaOCl solution (11.4 mmol) plus methanol. [i] Average of four runs. [j] $EtOCO_2Me$. [k] % yield based on complete conversion of azo to nitrogen. [l] $MeOCO_2Me$, 6%; CO_2, 31%.

of ethyl formate were also present, initially this was thought to confirm the involvement of such a pathway in the reaction of DCU with alkoxide, since formate esters were observed in that case as well. Ethyl formate may result from decomposition[28b] of ethoxycarbonyldiazene (**16**) (Scheme II). On the other hand, as pointed out in an earlier section, the source of methyl formate in the DCU system now appears to be oxidation of methanol by positive chlorine.

If an azo intermediate were actually involved in the DCU reaction, the corresponding hydrazide (**15**) should be produced as in the decomposition of **14** just discussed. However, in the presence of positive chlorine, **15** would be rapidly reoxidized. This hypothesis was confirmed by exposing **14** to sodium hypochlorite in methanol. Almost 90% of the nitrogen of the azo compound was liberated as N_2.

A crucial experiment was performed bearing upon this general approach. Potassium monochlorourethane is a stable, easily prepared compound. Bringing the salt and DCU together under the reaction conditions should give diethyl azodicarboxylate (**14**) according to the hypothesis expressed in Scheme II. The actual product, however, was *N*-monochlorourethane in 64% yield based on eq 11. Potassium chloride was isolated in 77% yield. This finding clearly demonstrates that Scheme II does not pertain and is corroborated by other data.[26]

$$1 + EtO_2CNCl^-K^+ \longrightarrow 2EtO_2CNHCl + KCl \qquad (11)$$

C. In view of the striking similarity in products from azo ester decomposition and from DCU, we surmised that perhaps the azo intermediate was indeed present but formed by a different route. With this in mind, an *N*-chloro nitrogen radical **17** was considered, eq 12. Dimerization of **17** establishes the nitrogen–nitrogen bond of **13**, and from this point the mechanism is identical with Scheme II. The difficulty is to rationalize formation of **17** from **1** in the presence of base. DCU is known to undergo homolysis induced by olefins,[5] with only a minute concentration of radicals being required to initiate the chain reaction. In the present case, reaction only occurs when base is added and is not complete until a stoichiometric amount of base is provided. At this point of development, work by Russell becomes relevant. His group demonstrated that carbanions or nitranions were capable of one-electron transfer to unsaturated molecules such as nitro aromatics, azobenzene, and diaryl ketones.[30] Russell also pointed out that alkyl and some aryl halides react with a number of organometallic reagents by a similar process (eq 13). These ideas may be applied to the present situation by viewing methoxide as the electron donor, while the dichloroamino group is the electron acceptor, as illustrated in eq 14. Further literature analogy is provided by the formation of Hofmann-Löffler type products in strongly basic systems from appropriate *N*-chloro compounds, such as (22*R*,25*S*)-*N*-chloro-22,26-imino-5α-cholestan-3β-ol[31] and *N*,*N*-dichloro-tri-*n*-butylcarbinamine.[32] These results lend additional credence to the postulate that radicals might be generated in the presence of strong base.

$$1 \longrightarrow \underset{17}{EtO_2CNCl} \xrightarrow{\text{dimerize}}$$

$$13 \xrightarrow{-Cl_2} 14 \longrightarrow EtO_2COMe + N_2 \qquad (12)$$

$$R + R'X \longrightarrow R + R + X \qquad (13)$$

$$1 + MeO^- \longrightarrow 17 + MeO\cdot + Cl^- \qquad (14)$$

In an attempt to gain supportive evidence for this scheme, DCU was exposed to Tollen's silver and to ferrous sulfate. Atomic silver is known to promote radical reactions of *N*-chloro secondary amines,[33] and ferrous salt has been demonstrated to be an effective radical initiator with *N*-chloroammonium salts.[34] However, neither the silver nor the iron salt produced a reaction resembling eq 12. In both cases, intractable mixtures resulted.

It should be noted that a homolytic pathway is inconsistent with the results from the DCU-^{15}N experiment discussed in section A. Hence, the labeling experiment constitutes strong evidence against the radical mechanism of eq 12.

Experimental Section

Materials. In general, high purity commercial chemicals were used without further purification. Urethane was obtained from Aldrich Chemical Co. and ammonium-^{15}N chloride from Stohler Isotope Chemicals Co.

Analytical Procedures. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer with neat samples or with potassium bromide pellets using the 1601.8-cm^{-1} band of polystyrene for calibration. Nmr spectra were taken with a Varian T-60 instrument and are reported in parts per million relative to tetramethylsilane as internal standard. Gas chromatography was conducted on a Varian Aerograph Hi-Fy 1720 by means of the indicated columns (10 ft × 0.25 in., copper) (column number, packing): (1) 20% Carbowax 20M on Chromosorb W (45–60 mesh); (2) molecular sieve 5A (30–60 mesh), 5 ft × 0.25 in.). Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E spectrometer.

Quantitative glpc was accomplished by comparison of peak areas of solutions of crude products with those of solutions of authentic materials. Positive chlorine content of preparations of *N*-chloro compounds was determined by standard iodometric titration.[35] Melting and boiling points are uncorrected.

***N*,*N*-Dichlorourethane.** A solution of urethane (44.5 g, 0.5 mol) in concentrated hydrochloric acid (75 ml) was added during 40 min with stirring to a suspension of calcium hypochlorite (70%, 204 g, 1 mol) in water (750 ml) at 0–10°. After additional concentrated hydrochloric acid (35 ml) was added during 10 min to dissolve the remaining calcium hypochlorite, the two-phase, translucent yellow mixture was stirred for 1 hr at 0°. The crude product was extracted with methylene chloride (2 × 100 ml), washed with water (200 ml), and dried with sodium sulfate. Removal of solvent under reduced pressure left a yellow oil which was distilled to afford 38 g (48%) of yellow, liquid product, bp 44–45° (6 mm), n^{23}D 1.4601 [lit.[5] bp 74–76° (15 mm), n^{26}D 1.4582]; ir (neat) 1753 (C=O), 1230 (CO), 1100, 1047, 993, 900, 827, 803, 766, and 735 cm^{-1}; nmr (CCl_4) δ 1.39 (t, 3 H, CH_3) and 4.37 (q, 2 H, CH_2).

Anal. Calcd for $C_3H_5Cl_2NO_2$: Cl, 44.9; Found: Cl, 44.7 (iodometric titration).

***N*-Monochlorourethane.** A literature procedure[17] was followed to yield 60% of colorless liquid, bp 43–43.5° (0.25 mm), n^{25}D 1.4454 [lit.[16] bp 45° (0.2 mm), n^{25}D 1.4435].

Anal. Calcd for $C_3H_5ClNO_2$: Cl, 29.0; Found: Cl, 27.0 (iodometric titration).

Potassium Monochlorourethane. A previous procedure[16] yielded 85% of anhydrous potassium salt.

Anal. Calcd for $C_3H_5ClKNO_2$: Cl, 22.0; Found: Cl, 21.8 (iodometric titration).

Urethane-^{15}N. A previously described procedure,[36] with ammonium chloride containing 95% ^{15}N, provided 76% of colorless needles, mp 46–48° (lit.[36] mp 47–48°).

N,N-Dichlorourethane-^{15}N. To a suspension of urethane-^{15}N (1.23 g, 13.8 mmol) and calcium hypochlorite (70%, 5.6 g, 28 mmol) in methylene chloride (40 ml) was added enough dilute hydrochloric acid (12%, 18 ml) during 30 min to dissolve all of the hypochlorite. The two-phase, translucent yellow mixture was stirred at 0° for 1 hr, and then the layers were separated. The organic phase was dried with magnesium sulfate, and then solvent was removed under reduced pressure to afford 2.1 g (85%) of the product. Iodometry indicated 90.5% of the theoretical amount of positive chlorine.

N,N-Dichlorocarbamates with Sodium Methoxide. The following procedure, with DCU as an example, was used in all cases. A solution of sodium methoxide (25 mmol) in methanol (18 ml) was added during 40 min to a solution of DCU (2.0 g, 12.5 mmol) in methanol (12 ml) at 0°. Volume changes were monitored with a gas buret. The reaction mixture was stirred for 45 min, and then volatile products were analyzed by glpc (column 1). The off-gas was analyzed by gc (column 2).

DCU-^{15}N and Isopropyl N,N-Difluorocarbamate with Sodium Methoxide. In a system thoroughly flushed with helium, a solution of sodium methoxide (19.6 mmol) in methanol (10 ml) was added during 25 min to a solution of DCU-^{15}N (1.14 g, 6.55 mmol) and isopropyl N,N-difluorocarbamate (0.91 g, 6.55 mmol) in methanol (10 ml) at 0°. The evolved gases were collected over water. The liquid reaction mixture was analyzed by glpc (column 1). The off-gas was analyzed by gc (column 2) and by mass spectrometry. A strong peak at m/e 85 was attributed[25] to SiF_3^+, a fragment ion from SiF_4 which most likely arose from attack of hydrofluoric acid on the glass of the reaction vessel. The flask was etched.

Diethyl Azodicarboxylate with Sodium Ethoxide. Sodium (0.13 g, 5.7 mg-atoms) was dissolved in absolute ethanol (10 ml). The resulting sodium ethoxide solution was immediately added to a solution of diethyl azodicarboxylate (1 g, 5.7 mmol) in ethanol (20 ml) during 1.5 min at 0°. The vigorous reaction which ensued shortly after the first drops were added was complete within a few minutes. Volume changes were monitored with a gas buret. Gc of the off-gas indicated only nitrogen and atmospheric oxygen (column 2). After analysis for diethyl carbonate by glpc (column 1), the reaction mixture was acidified, causing the orange color to disappear and precipitating sodium chloride. After the salt was filtered off, the filtrate was evaporated to dryness under reduced pressure, leaving 0.43 g (86%) of a slightly yellow solid, mp 115–130°. The ir spectrum of this material was identical with that of authentic diethyl hydrazinedicarboxylate. Recrystallization from water provided a white powder, mp 129–132° (lit.[29] mp 134–135°).

Potassium Monochlorourethane with DCU. To a solution of DCU (1.0 g, 6.3 mmol) in methanol (20 ml) at 0° was added a solution of anhydrous potassium monochlorourethane (1.0 g, 6.3 mmol) in methanol (20 ml) during 1 hr. After the mixture was stirred for 40 min, potassium chloride was filtered off (0.4 g, 77%), and the filtrate was freed of methanol under reduced pressure. The resultant slightly yellow oil (1.0 g, 64%) gave an ir spectrum identical with that of authentic N-monochlorourethane.

Ethyl Methyl Carbonate. Sodium (5 g, 0.22 g-atom) was dissolved in 60 ml of absolute methanol, and the solution was then added slowly with stirring at −20° to ethyl chloroformate (20.5 g, 0.19 mol). After the mixture had warmed to room temperature, 10% potassium carbonate (50 ml) was added, and the organic layer was separated and dried over calcium chloride. Distillation provided 9.7 g (49%) of ester, bp 105–109°, n^{23}D 1.3768 (lit.[37] bp 107°, lit.[38] n^{20}D 1.3782); ir (neat) 1751 (C=O), 1285 (CO), 1119, 1095, 1014, 942, 882, and 797 cm^{-1}; nmr (CCl_4) δ 1.27 (t, 3 H, CH_2CH_3), 3.70 (s, 3 H, OCH_3), and 4.13 (q, 2 H, CH_2).

Stability of Positive Chlorine in Methanol. A. DCU. A sample of DCU was dissolved in methanol at room temperature. Aliquots were analyzed for positive chlorine at intervals. After 60 min, 98% of the original positive chlorine remained.

B. Sodium Hypochlorite. Sodium hypochlorite (0.79 M, 16 ml) was mixed with methanol (44 ml) and kept at 0°. Aliquots were analyzed for positive chlorine at intervals. After 60 min, 95% of the original positive chlorine remained.

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