gram-atoms O^{18} in ROY $= f_1x + f_n(1 - x)$
gram-atoms O^{18} in $CO_2 = 2f_n x + f_1(1 - x) + f_n(1 - x) = f_nx + f_1 + f_n - f_1x$
Total gram atoms $O^{18} = 2f_n + f_1$
gram-atoms O^{16} in ROY $= x(1 - f_1) + (1 - x)(1 - f_n)$
gram-atoms O^{16} in $CO_2 = 2x(1 - f_n) + (1 - x)(1 - f_1) + (1 - x)(1 - f_n)$
total gram-atoms $O^{16} = 3 - 2f_n - f_1$

$$\text{g.a. } O^{18} \text{ in ROY} = f_1' = f_1x + f_n(1 - x) \qquad (2)$$

moles CO_2^{46} = gram-atoms O^{18} in $CO_2 = f_nx + f_1 + f_n - f_1x$
moles CO_2^{44} = total moles CO_2 − moles O^{18}

$$= \frac{\text{total gram-atoms O in } CO_2}{2} - \text{g.a. } O^{18} \text{ in } CO_2$$

$$= \frac{\text{g.a. } O^{16} \text{ in } CO_2 - \text{g.a. } O^{18} \text{ in } CO_2}{2}$$

$$\frac{\text{moles } CO_2^{46}}{\text{moles } CO_2^{44}} = \frac{46}{44} \text{ peak ratio in mass spectrometer} =$$

$$\frac{2 \text{ g.a. } O^{18}}{\text{g.a. } O^{16} - \text{g.a. } O^{18}} = \frac{f_nx + f_1 + f_n - f_1x}{1 - f_1 + f_1x - f_nx - f_n} \qquad (1)$$

It is necessary to derive an additional formula in order to calculate f_1 from R_1, the 46/44 mass ratio of the CO_2 obtained in the decomposition of the alkyl chloroformate

$$\text{ROCOCl} \xrightarrow{\text{pyridine}} \text{RCl} + CO_2$$

g.a. $O^{18} = f_1 + f_n$
g.a. $O^{16} = 2 - f_1 - f_n$
no. of moles CO_2^{46} = g.a. $O^{18} = f_1 + f_n$
no. of moles $CO_2^{44} = 1 - f_1 - f_n$

$$R_1 = \frac{f_1 + f_n}{1 - f_1 - f_n} \qquad (3)$$

Calculation of x
46/44 peak ratio = 0.00551, $R_1 = 0.00974$, $f_n = 0.00206$

from formula 3, $f_1 = 0.00759$
from formula 1, $x = 0.754$
from formula 2, $f_1' = 0.00623$
from the assay on CO_2 sample 4 (see Fig. 1), R_1, the 46/44 mass ratio = 0.00844

From this and formula 3 the value of $f_1' = 0.00630$ is calculated. This checks reasonably well with the value for f_1' calculated above.

Acknowledgment.—The author is extremely grateful to Dr. S. Ruven Smith, who supervised the mass spectral work and helped to interpret the mass spectral data. The coöperation of Mr. Joseph Johnson, who operated the mass spectrometer, and of Mrs. H. R. Young, who reduced the mass spectral data, are sincerely appreciated. The author also wishes to thank Professor W. H. Urry, who reviewed this paper and supplied several very helpful suggestions.

CHINA LAKE, CALIF.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE TEST STATION]

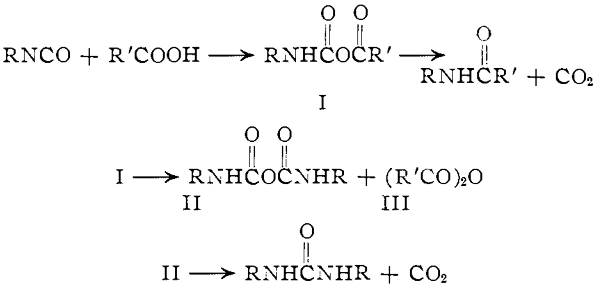
The Reaction of Dialkylcarbamyl Chlorides with Silver Nitrate[1]

BY WILLIAM P. NORRIS

RECEIVED JUNE 16, 1958

Dialkylcarbamyl chlorides react with silver nitrate to give the corresponding dialkylnitramines and dialkylnitrosamines plus carbon dioxide and other products. Silver nitrite and dimethylcarbamyl chloride give dimethylnitrosamine plus carbon dioxide and other products. The reactions presumably proceed through unstable intermediate dialkylcarbamyl nitrates or nitrites to give nitramines or nitrosamines, respectively. The rate of evolution of carbon dioxide obeyed the first-order rate law wherever measured.

Isocyanates react with carboxylic acids to give intermediate carbamyl carboxylates I. The mixed anhydride I can disproportionate to the pure anhydrides II and III with the former losing carbon dioxide to give a disubstituted urea, or the mixed anhydride I can lose carbon dioxide directly to give a substituted amide.[2,3] Aliphatic isocyanates usually give amides and aromatic isocyanates give chiefly disubstituted ureas. The strong acids, HCOOH, Cl_3CCOOH and $NCCH_2COOH$, generally give better yields of amides than the weaker acids, *i.e.*, straight aliphatic acids. Lower temperatures and lower concentrations increased amide yield and decreased the yield of urea. Aliphatic isocyanates react with fuming sulfuric acid to form alkylcarbamyl sulfuric acids which lose carbon dioxide to give alkylsulfamic acids.[4] A boronic acid and an alkyl isocyanate in the presence of a tertiary amine react to give a boronalkylamide and carbon dioxide.[5]



$$\text{RNCO} + \text{R'COOH} \longrightarrow \underset{\text{I}}{\text{RNH}\overset{O}{\overset{\|}{C}}\text{O}\overset{O}{\overset{\|}{C}}\text{R'}} \longrightarrow \text{RNH}\overset{O}{\overset{\|}{C}}\text{R'} + CO_2$$

$$\text{I} \longrightarrow \underset{\text{II}}{\text{RNH}\overset{O}{\overset{\|}{C}}\text{O}\overset{O}{\overset{\|}{C}}\text{NHR}} + \underset{\text{III}}{(\text{R'CO})_2\text{O}}$$

$$\text{II} \longrightarrow \text{RNH}\overset{O}{\overset{\|}{C}}\text{NHR} + CO_2$$

$$R_2BOH + R'NCO \longrightarrow R_2BNHR' + CO_2$$

It is suggested that the above reactions all proceed through an unstable intermediate, of the general formula $\text{RR'N}\overset{O}{\overset{\|}{C}}\text{X}$ (IV), where R = alkyl or aryl, R′ = H and X = $\overset{O}{\overset{\|}{C}}\text{R}$, SO_3H and $B(OR)_2$. The present work extends the reaction to systems where R and R′ = alkyl and X = NO_2 or NO, affords a new synthetic route to dialkylnitramines and nitrosamines, and at the same time

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(1) Presented in part before the Pacific Southwest Meeting of the American Chemical Society, San Diego, Calif., April 27, 1957.

(2) C. Naegeli and A. Tyabji, *Helv. Chim. Acta*, **17**, 931 (1934).

(3) R. G. Arnold, J. A. Nelson and J. J. Verbanc, *Chem. Revs.*, **57**, 52 (1957).

(4) T. I. Bieber, THIS JOURNAL, **75**, 1405 (1953).

(5) R. W. Upson, U. S. Patent 2,517,944; *C. A.*, **44**, 10378a (1950).

provides information which may help elucidate the mechanism of amide formation from IV.

Dialkylcarbamyl chloride reacts with silver nitrate in dry acetonitrile or carbon tetrachloride presumably to give an unstable dialkylcarbamyl nitrate which, in turn, reacts to give dialkylnitramine, dialkylnitrosamine, carbon dioxide and a little dialkylammonium nitrate. Except where otherwise indicated the yield values in Table I represent material actually isolated in a relatively pure condition. Recrystallization of the solid nitramines, dimethyl-, di-(β-cyanoethyl)- and 3-oxapentamethylene-, resulted in heavy loss of nitramine so that actually the crude yield figures are probably a better basis for comparing the reaction performance of the various carbamyl chlorides than the purified yield figures would be. The liquid nitramines and nitrosamines were separated by distillation and extraction techniques and the yields listed are probably quite close to the actual yields. The highest yield of nitramine was obtained from dimethylcarbamyl chloride, followed in order by di-(β-cyanoethyl)-, diisopropyl-, 3-oxapentamethylene-, diethyl- and di-*n*-propylcarbamyl chloride. In the case of the latter two, extensive tar formation occurred in the reaction. Using carbon tetrachloride as a reaction medium instead of acetonitrile almost doubled the nitramine yield in the case of di-*n*-propylcarbamyl chloride. Diethylammonium nitrate and di-*n*-propylammonium nitrate were isolated in small amounts from the non-volatile residues of the reaction products of the respective carbamyl chlorides. Small amounts of dialkylammonium nitrates were no doubt present in the water-soluble residues in the other cases too, but no attempt was made to isolate them.

TABLE I

YIELDS OF R_2NNO_2 AND R_2NNO FROM THE REACTION OF R_2NCOCl WITH $AgNO_3$

R_2	Solvent	% R_2NNO_2	% R_2NNO
$(CH_3)_2$	CH_3CN	48 (70% crude)	11
$(C_2H_5)_2$	CH_3CN	28	29
$[(CH_3)_2CH]_2$	CH_3CN	49 (53% crude)	29[a]
$(CH_3CH_2CH_2)_2$	CH_3CN	14	28
$O(CH_2CH_2)_2$	CH_3CN	22 (44% crude)	40[a]
$(NCCH_2CH_2)_2$	CH_3CN	30 (59% crude)	26[a]
$(CH_3CH_2CH_2)_2$	CCl_4	25	39

[a] This nitrosamine was not isolated and purified but was assumed to be the difference between ether-soluble crude product and crude nitramine.

Dimethylcarbamyl chloride reacted with silver nitrite in acetonitrile to give a 66% yield of dimethylnitrosamine.

The availability of silver nitrate and silver nitrite and ease of preparation of carbamyl chlorides may make this reaction of preparative value for secondary nitramines and nitrosamines, especially in cases where the reaction conditions of existing syntheses may be objectionable.[6]

The gaseous reaction products from several carbamyl chloride and silver nitrate reactions were analyzed on a mass spectrometer and the compositions are given in Table II. Carbon dioxide is the principal gaseous product. In one case an 8.5% yield of nitrous oxide was obtained but, since only one observation was made, the significance of this observation is open to question. Nitrous oxide is formed by reaction of mineral acids with primary nitramines but not with simple secondary nitramines.[7] The origin of the nitrous oxide remains unknown.

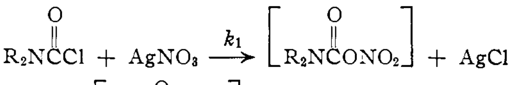
TABLE II

ANALYSES OF GASEOUS PRODUCTS FROM THE REACTION OF R_2NCOCl WITH $AgNO_3$[a]

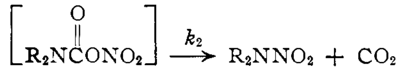
R	Solvent	% CO_2	% NO	% N_2O
CH_3	CH_3CN	99.0	1.0	
C_2H_5[b]	CH_3CN	91.0		8.5
$(CH_3)_2CH$[c]	CH_3CN	97.5	1.0	1.0
$CH_3CH_2CH_2$	CCl_4	99.0	1.0	

[a] Analyses were made on a mass spectrometer by Dr. S. Ruven Smith of this Laboratory. [b] Other product ethylene. [c] Other product propylene.

The first reaction to take place between a carbamyl chloride and silver nitrate is the precipitation of silver chloride and the formation of the postulated intermediate carbamyl nitrate. In the case of dimethylcarbamyl chloride in acetonitrile the reaction was found to be first-order in silver nitrate and first-order in carbamyl chloride and at 38.90 ± 0.03°, $k_1 = 1.5 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$. The calculated half-life for 0.100 *N* solutions of reactants was eleven minutes. By increasing the concentration of one reactant (dimethylcarbamyl chloride) to 1.00 *N* the calculated half-life is reduced to forty-six seconds. This is a relatively short time compared to the half-life for the evolution of gas. By this means the first reaction, at the latter concentrations, is made sufficiently fast so that a plot of ln $(V_\infty - V_t)$ *versus* t gave a straight line (V_∞ = volume of gas evolved when the reaction is complete, V_t = volume of gas measured at any given time, t). Straight lines were obtained out to at least two half-lives. The obedience of the rate of gas evolution to the first-order rate law can be interpreted to mean that the reactions of dimethylcarbamyl nitrate are first-order or pseudo first-order reactions and that any gas-producing reactions other than step 2 are fast compared to step 2. Dimethylcarbamyl nitrite (the proposed intermediate in the silver nitrite–dimethylcarbamyl chloride reaction), which may be an intermediate in the formation of dimethylnitrosamine in the dimethylcarbamyl chloride–silver nitrate reaction, decomposes by a first-order reaction and is fast compared to step 2 (see Table III).



$$R_2N\overset{O}{\overset{\|}{C}}Cl + AgNO_3 \xrightarrow{k_1} \left[R_2N\overset{O}{\overset{\|}{C}}ONO_2\right] + AgCl \qquad (1)$$



$$\left[R_2N\overset{O}{\overset{\|}{C}}ONO_2\right] \xrightarrow{k_2} R_2NNO_2 + CO_2 \qquad (2)$$

The rates of gas evolution from the decomposition of diethyl- and diisopropylcarbamyl nitrates

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(6) Other nitramine syntheses will be found in the references: (a) W. J. Chute, K. G. Herring, L. E. Tombs and G. F Wright, *Can. J. Research*, **B26**, 89 (1948); (b) J. H. Robson, THIS JOURNAL, **77**, 107 (1955); (c) W. D. Emmons, *ibid.*, **76**, 3468 (1954); (d) W. D. Emmons and J. P. Freeman, *ibid.*, **77**, 4387 (1955); (e) W. D. Emmons, A. S. Pagano and T. E. Stevens, *J. Org. Chem.*, **23**, 311 (1958); (f) A. H. Lamberton, *Quart. Revs.*, **5**, 75 (1951).

(7) H. van Erp, *Rec. trav. chim.*, **14**, 40 (1895).

TABLE III

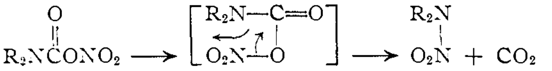
RATES OF GAS EVOLUTION FROM REACTION OF R_2NCOCl (1.00 N) WITH $AgNO_3$ (0.100 N) OR $AgNO_2$ (0.100 N) IN CH_3CN AT 38.90 ± 0.03°[a,b]

R_2	Silver salt	k, sec.$^{-1}$	CO_2 yield, %
$(CH_3)_2$	$AgNO_3$	2.9×10^{-3}	42
$(C_2H_5)_2$	$AgNO_3$	1.6×10^{-4}	45
$[(CH_3)_2CH]_2$	$AgNO_3$	1.1×10^{-3}	77
$O(CH_2CH_2)_2$	$AgNO_3$	1.5×10^{-3}	40
$(CH_3)_2$	$AgNO_2$	1.2×10^{-2}	29

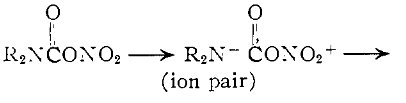
[a] The rate constants, *k*, are averages of at least two runs in each case that agreed to within 3% of each other. [b] The values of *k* are those obtained directly from the ln $(V_\infty - V_t)/t$ plot.

were measured and found to obey the first-order rate law. The rate of reaction of morpholine carbonyl chloride with silver nitrate was sufficiently slow so that even with a 1.00 N solution of the carbonyl chloride a first-order plot of the gas evolution did not give a straight line. The rate of silver chloride deposition was measured at 38.90 ± 0.03° using 1.00 N morpholine carbonyl chloride and 0.100 N silver nitrate in acetonitrile. This gave a pseudo first-order rate constant of 9.8×10^{-3} sec.$^{-1}$. The first-order rate constant for gas evolution was then determined from the equation given by Chien[8] for consecutive first-order reactions. Di-(β-cyanoethyl)-carbamyl chloride reacted quite slowly with silver nitrate and it was necessary to reflux the acetonitrile solution for three hours to assure complete precipitation of silver chloride.

A cyclic mechanism similar to that proposed by Bieber[4] for the decomposition of his intermediate alkylcarbamyl sulfuric acid could also apply in the cases of the proposed intermediate dialkylcarbamyl nitrates. The same sort of mechanism could be written for dialkylcarbamyl nitrites.

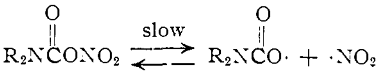


Another mechanism to be considered is one similar to Cram's[9] SNi mechanism for the decomposition of alkyl chlorosulfites involving ion pair intermediates. This mechanism has the advantage of not requiring the formation of the highly strained four-membered ring transition state of the previous mechanism. Both proposed mechanisms are first-order reactions and are therefore compatible with the measured first-order kinetics of gas evolution. It is not possible to eliminate either mechanism on the basis of information now available. Careful investigation of this reaction using other systems such as dialkylcarbamyl trifluoroacetates or the corresponding tosylates, where oxidation-reduction reactions would be less prevalent than in the nitrate and nitrite systems, could no doubt throw much light on the situation.

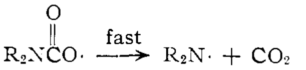


$$\mathrm{R_2N\overset{\overset{O}{\|}}{C}ONO_2 \longrightarrow \underset{(ion\ pair)}{R_2N^-\ \overset{\overset{O}{\|}}{C}ONO_2{}^+} \longrightarrow}$$
$$\mathrm{\underset{(ion\ pair)}{R_2N^-\ \ NO_2{}^+} + CO_2 \longrightarrow R_2NNO_2 + CO_2}$$

Finally, the possibility that amide formation from dialkylcarbamylnitrate occurred by a free radical reaction was investigated. Nitrogen dioxide was added to diisopropylcarbamyl nitrate in carbon tetrachloride with the thought that more nitramine might be formed if the reaction proceeded as shown in step 5. Only a small yield of unidentified higher boiling material showing nitro group absorption in the infrared spectrum was obtained. In another experiment, dimethylcarbamyl chloride and silver nitrate in acetonitrile solution were allowed to react in the presence of nitric oxide. The gas and liquid phases suddenly turned brown at 40° and the temperature rose rapidly to 60° and gas evolution was very vigorous even though a Dry Ice-acetone cooling bath was used. The presence of nitric oxide increased the yield of dimethylnitrosamine at the expense of dimethylnitramine as would be expected if the reaction went by a free radical mechanism. In none of the normal reactions, however, was the brown color of nitrogen dioxide ever observed and only trace amounts of nitric oxide occurred in the gases evolved. It seems probable that if nitric oxide and nitrogen dioxide were intermediates, then some nitrogen dioxide (brown color) would have been evident in all the reactions. So despite the increased yield of dimethylnitrosamine obtained when the reaction is run in the presence of nitric oxide it is not likely that nitric oxide and nitrogen dioxide are normally intermediates in the decomposition of dialkylcarbamyl nitrates to nitramines and nitrosamines, and therefore the reaction probably does not go by a free radical mechanism.



$$\mathrm{R_2N\overset{\overset{O}{\|}}{C}ONO_2 \overset{slow}{\rightleftarrows} R_2N\overset{\overset{O}{\|}}{C}O\cdot + \cdot NO_2} \qquad (3)$$



$$\mathrm{R_2N\overset{\overset{O}{\|}}{C}O\cdot \xrightarrow{fast} R_2N\cdot + CO_2} \qquad (4)$$

$$\mathrm{R_2N\cdot + \cdot NO_2 \xrightarrow{fast} R_2NNO_2} \qquad (5)$$

Experimental

Dimethylcarbamyl Chloride and Silver Nitrate in Acetonitrile.—Fifty-one grams (0.30 mole) of silver nitrate was dissolved in 100 ml. of dry acetonitrile[10] and added to 32.3 g. (0.30 mole) of dimethylcarbamyl chloride dissolved in 200 ml. of dry acetonitrile. Silver chloride precipitated immediately. The reaction mixture warmed spontaneously. At 40° gas evolution became vigorous. The temperature was prevented from rising above 50° by means of external cooling. After about five minutes the temperature began to drop slowly. The reaction mixture was allowed to stand for two days at 25° before work up. Forty-three grams (100% yield) of silver chloride was filtered off. The acetonitrile was distilled from the filtrate at 100 mm. pressure through a two foot, glass helices packed column. There was 27 g. of yellow oil remaining in the still-pot. Two and one-half grams (11% yield) of dimethylnitrosamine, b.p. 82–90° at 100 mm. pressure, was removed from the yellow oil by fractionation through a low hold-up, precision distillation column rated at 90 theoretical plates.[11] The res-

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[8] J. Chien, THIS JOURNAL, **70**, 2256 (1948).

[9] D. J. Cram, *ibid.*, **75**, 332 (1953).

[10] Calcium hydride is a very effective agent for drying acetonitrile. There was no detectable reaction between the acetonitrile and calcium hydride even after two days at reflux temperature.

[11] The identities of the various liquid nitrosamines were confirmed by comparison of their infrared spectra with those of dialkylnitrosamines prepared by direct nitrosation of dialkylamines. The identities of the liquid nitramines were established similarly using samples of nitramines prepared by the method of Robson [b] as reference materials.

idue in the still-pot was extracted with ether and the ether evaporated to leave 19 g. (70% yield) of impure dimethylnitramine, m.p. 45–53°. Recrystallization from ether gave 13 g. (48% yield) of dimethylnitramine, m.p. 54–56°.[12]

Diethylcarbamyl Chloride and Silver Nitrate in Acetonitrile.—The reaction was carried out exactly the same as the previous one up to the point where the silver chloride was filtered off. The acetonitrile filtrate was distilled at 30 mm. pressure. The residue was partially distilled at 0.5 mm. pressure to give 20 g. of liquid, b.p. 34–45°. There was 14 g. of dark residue in the still-pot. The distillate was dissolved in 100 ml. of carbon tetrachloride and extracted with 30 ml. of concentrated hydrochloric acid. The carbon tetrachloride phase was separated and distilled to give 4.7 g. of diethylnitramine, b.p. 115–118° at 50 mm. pressure.[11] The hydrochloric acid phase was neutralized with 50% sodium hydroxide solution and extracted with ether. The ether was evaporated and the residue was distilled at 50 mm. pressure to give 9 g. of liquid, b.p. 75–115° which, on the basis of its refractive index, contained 7.1 g. (29% yield) of diethylnitrosamine and 1.9 g. of diethylnitramine. This made a total nitramine yield of 6.6 g. (28% yield). The dark solid residue (14 g.) from the initial distillation was recrystallized from tetrahydrofuran to give 4 g. of water-soluble, white plates, m.p. 102–105°. Another recrystallization raised the melting point to 103–105°. An infrared spectrum of the solid was identical with that of a sample of diethylammonium nitrate.

Diisopropylcarbamyl Chloride and Silver Nitrate in Acetonitrile.—Thirty grams (0.175 mole) of silver nitrate was dissolved in 75 ml. of dry acetonitrile and added to 28.8 g. (0.175 mole) of diisopropylcarbamyl chloride in 125 ml. of dry acetonitrile. Silver chloride precipitated immediately. After about two minutes gas evolution began and the reaction mixture began heating up. The temperature was prevented from rising above 50° by means of external cooling. After ten minutes gas evolution was quite slow. The reaction mixture stood for two days at 25° before work up. The silver chloride (quantitative yield) was filtered off and the acetonitrile removed at 30 mm. pressure to leave 29 g. of dark brown liquid product. This product was extracted with two 100-ml. portions of ether. Evaporation of the ether left 19 g. of yellow crystalline material which was triturated with 50 ml. of concentrated hydrochloric acid. The remaining solid was filtered off and washed with water to give 12 g. of impure diisopropylnitramine, m.p. 98–102°. The nitramine was dissolved in 20 ml. of 70% nitric acid and then precipitated by addition of 100 ml. of water to give 11 g. (43% theory) of diisopropylnitramine, m.p. 104–106° (lit.[13] m.p. 107–108°). The concentrated hydrochloric acid solution was neutralized with 20% sodium hydroxide solution while keeping the temperature below 20°. Four grams of solid separated. This was dried and then dissolved in 50 ml. of ether saturated with hydrogen chloride. After 24 hours 2 g. of diisopropylammonium chloride, m.p. 210–213°, separated. Evaporation of the ether and hydrogen chloride left 1.5 g. of diisopropylnitramine, m.p. 105–107°, for a total nitramine yield of 12.5 g. (49% yield). The diisopropylnitrosamine was completely destroyed. Assuming that all the ether-soluble material (19 g.) obtained in the initial product extraction was either diisopropylnitramine or diisopropylnitrosamine then there was 6.5 g. (29% yield) of diisopropylnitrosamine. The ether-insoluble residue from the initial reaction mixture was almost entirely soluble in water and presumably contained diisopropylammonium nitrate analogous to the case of the water soluble residue from the diethylcarbamyl chloride–silver nitrate reaction.

Di-*n*-propylcarbamyl Chloride and Silver Nitrate in Acetonitrile.—Fifty-one grams (0.300 mole) of silver nitrate was dissolved in 100 ml. of dry acetonitrile and was added to 45.6 g. (0.278 mole) of di-*n*-propylcarbamyl chloride in 200 ml. of acetonitrile. Silver chloride began precipitating immediately but gas evolution was slow until the reaction mixture had been heated to 60°. When gas evolution ceased, precipitated silver chloride (quantitative yield) was filtered off and the acetonitrile removed under reduced pressure. Distillation of the product at 0.1 mm. pressure gave 22 g. of material, b.p. 35–50°, and 21 g. of dark brown residue remained in the still-pot. The distillate was extracted with three 25-ml. portions of concentrated hydrochloric acid. The organic phase was taken up in methylene chloride and washed with two 10-ml. portions of cold water. Evaporation of the methylene chloride left 6.0 g. (14% yield) of di-*n*-propylnitramine.[11] The concentrated hydrochloric acid extracts were combined and diluted with 50 ml. of water then neutralized to a methyl orange end-point with 50% sodium hydroxide solution. Extraction of the neutralized aqueous phase with two 50-ml. portions of ether and evaporation of the ether gave 10 g. (28% yield) of di-*n*-propylnitrosamine.[11] The 21 g. of distillation residue from above was dissolved in water and made strongly basic with sodium hydroxide and steam distilled. The steam distillate was extracted with ether and the ether evaporated to give 3.0 g. of di-*n*-propylamine, b.p. 100–105° at 705 mm. pressure. The melting point of the hydrochloride salt of the amine was 269–271° and showed no depression when a mixed melting point was taken with an authentic sample of di-*n*-propylammonium chloride. The amine was probably in the distillation residue as the nitrate salt as was the case with the diethylamine in a previous experiment.

Di-*n*-propylcarbamyl Chloride and Silver Nitrate in Carbon Tetrachloride.—Fifty-one grams (0.300 mole) of silver nitrate was ground to a powder and added to 200 ml. of dry carbon tetrachloride which contained 45.6 g. (0.278 mole) of di-*n*-propylcarbamyl chloride. The stirred reaction mixture was heated to 60° where gas evolution became noticeable. The reaction was maintained at 60° for two hours and was then heated to reflux for an additional two hours. The solid was filtered off and washed with carbon tetrachloride and then with water to give 40.0 g. (100% yield) of silver chloride. The carbon tetrachloride filtrate upon cooling deposited 3.5 g. of crystals. After recrystallizing from tetrahydrofuran the melting point was 150–153°. A mixed melting point with an authentic sample of di-*n*-propylammonium nitrate, m.p. 154–157°, was not depressed.

The carbon tetrachloride was removed from the filtrate under reduced pressure and the product distilled at 0.1 mm. pressure to give 26 g. of material, b.p. 44–55°. The nitramine and nitrosamine were separated as in the previous experiment to give 10 g. (25% yield) of di-*n*-propylnitramine[11] and 14 g. (39% yield) of di-*n*-propylnitrosamine.[11]

Morpholinecarbonyl Chloride and Silver Nitrate in Acetonitrile.—Thirty-four grams (0.200 mole) of silver nitrate and 29.9 g. (0.200 mole) of morpholinecarbonyl chloride were allowed to react following the procedure used for diisopropylcarbamyl chloride up to and including the point where the solvent is removed. The residue was distilled at 0.1 mm. pressure to give 21 g. of material, b.p. 45–55°. Nine grams of distillate was dissolved in ether and dry hydrogen chloride was passed into the solution until no more was absorbed. The solid was filtered off and the ether evaporated from the filtrate to leave 5 g. (44% yield) of crude N-nitromorpholine, m.p. 40–47°. Recrystallization from methanol gave 2.5 g. (22% yield) of material, m.p. 53–54°.[13]

Reaction of Di-(β-cyanoethyl)-carbamyl Chloride with Silver Nitrate in Acetonitrile.—To a solution of 1.70 g. (0.00100 mole) of silver nitrate in 20 ml. of dry acetonitrile was added 1.86 g. (0.00100 mole) of di-(β-cyanoethyl)-carbamyl chloride. Only after several minutes did silver chloride appear in the solution. The solution was refluxed for 3 hours. The silver chloride, 1.39 g. (97% yield), was filtered off. The acetonitrile was evaporated from the filtrate to leave 1.4 g. of partially solidified material. This material was dissolved in methylene chloride and treated with gaseous hydrogen chloride causing appearance of an insoluble oily layer. The methylene chloride solution was separated and the solvent evaporated to leave 1.0 g. (59% yield) of crude di-(β-cyanoethyl)-nitramine, m.p. 47–53°. Recrystallization from methanol–methylene chloride solvent gave 0.50 g. (30% yield), m.p. 53–55°.[14]

Dimethylcarbamyl Chloride and Silver Nitrite in Acetonitrile.—Forty-one grams (0.266 mole) of dry, freshly prepared silver nitrite was added portionwise to a stirred solution of 28.8 g. (0.266 mole) of dimethylcarbamyl chloride in 250 ml. of dry acetonitrile. The temperature rose to 40° and was maintained there with the aid of an ice-bath until the reaction was complete. The silver chloride (nearly quantitative yield) was filtered off. The volume of the filtrate was

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(12) O. Degner and H. v. Pechmann, *Ber.*, **30**, 647 (1897).

(13) G. S. Myers and G. F Wright, *Can. J. Research*, **B26**, 257 (1948).

(14) W. J. Chute, G. E. Dunn, J. C. MacKenzie, G. S. Myers, G. N. R. Smart, J. W. Suggitt and G. F Wright, *Can. J. Research*, **B26**, 114 (1948).

reduced by half by boiling off solvent at atmospheric pressure. The remainder of the solvent was removed by distillation through a one foot long Vigreux column at 100 mm. pressure and then the product was distilled at 20 mm. pressure to give 14.0 g., b.p. 50–60°. The product was distilled again at 20 mm. to give 13 g. (66% yield) of dimethylnitrosamine, b.p. 52–57°. An infrared spectrum of the material was practically identical with that of an authentic sample of dimethylnitrosamine except for a small absorption band at 6.04 μ. The contaminant was not identified but was shown not to be dimethylnitramine on the basis of infrared data.

Diisopropylcarbamyl Chloride and Silver Nitrate with Nitrogen Dioxide in Carbon Tetrachloride.—Five and one-tenth grams (0.030 mole) of powdered silver nitrate was added to 3.3 g. (0.020 mole) of diisopropylcarbamyl chloride dissolved in 50 ml. of carbon tetrachloride. Nitrogen dioxide was bubbled through the stirred reaction mixture. The reaction mixture was heated to 50° and held there for 20 minutes. The silver salts were filtered off, and the carbon tetrachloride evaporated. The residue was distilled at 2 mm. pressure to give 1.0 g. of liquid material, b.p. 82–85°. The elemental analyses were as follows: C, 42.47; H, 9.30; N, 20.52. These analyses do not correspond to those for either diisopropylnitramine or nitrosamine; furthermore, both of the latter compounds are solids.

Dimethylcarbamyl Chloride and Silver Nitrate in Acetonitrile in the Presence of Nitric Oxide.—Dry helium was passed through a 1000-ml. reaction vessel containing 32.3 g. (0.300 mole) of dimethylcarbamyl chloride in 200 ml. of dry acetonitrile to remove oxygen. Nitric oxide was then passed into the vigorously stirred solution for 5 minutes. While maintaining the nitric oxide atmosphere and the stirring, 51.0 g. (0.300 mole) of silver nitrate in 100 ml. of acetonitrile was added from an addition funnel. Silver chloride precipitated immediately and the temperature soon rose to 40°. Nitrogen dioxide then appeared in the gas and liquid phases and the temperature climbed rapidly to 70° even though a Dry Ice–acetone-bath was placed around the flask when the temperature reached 50°. The evolution of gas was so vigorous that a considerable amount of the reaction mixture was carried out of the flask. The temperature soon dropped to 50° where it was maintained for 5 minutes. The reaction was then worked up in exactly the same manner as in the experiment where no nitric oxide was used to give 8.7 g. (40% yield) of dimethylnitrosamine[11] and 10.6 g. (40% yield) of dimethylnitramine, m.p. 50–54°. Recrystallization from ether gave dimethylnitramine, m.p. 55–57°.

Analysis of Gases Evolved from the Reactions of Dialkylcarbamyl Chloride with Silver Nitrate.—Small samples (0.01 mole) of the appropriate carbamyl chloride was added to 0.01 mole of silver nitrate in 10 ml. of solvent in a closed system fitted with a gas buret for measuring the amount of gas evolved. The system was swept out with dry helium before the reactants were mixed. The gas samples were analyzed on a mass spectrometer by Dr. S. Ruven Smith of this Laboratory. The results are given in Table II in the text.

Measurements of Rates of Gas Evolution.—The standard silver salt solutions were made up by weighing reagent grade silver nitrate or dry freshly prepared silver nitrite into volumetric flasks and making up to volume with acetonitrile which had been distilled from calcium hydride. The carbamyl chlorides were distilled under reduced pressure and center cuts were used for making up standard solutions with dry acetonitrile. Five milliliter samples each of a silver salt solution and a carbamyl chloride solution were placed in separate legs of an inverted Y-tube arrangement which permitted mixing by tilting after the reactants had been thermally equilibrated with the constant temperature bath.[15] The reaction vessel was attached to a gas buret for measuring the volume of the evolved gas. The reaction mixture was constantly agitated to facilitate liberation of the gases. The gas volume due to solvent vapor was subtracted from the measured gas volume. The vapor pressure of acetonitrile at 38.90° was interpolated from a plot of the logarithm of the vapor pressure at various temperatures *versus* the reciprocal of the absolute temperature.[16]

TABLE IV

GAS VOLUME *versus* TIME DATA ON THE REACTION OF 5.0 ML. OF 2.0 N $(CH_3)_2NCOCl$ AND 5.0 ML. OF 0.20 N $AgNO_3$ ACETONITRILE SOLUTIONS AT 38.90 ± 0.03°[a]

Time, min.	V_t, ml. CO_2	$V_\infty - V_t$, ml.	Time, min.	V_t, ml. CO_2	$V_\infty - V_t$, ml.
0	0.0	12.2	7	8.6	3.6
1	1.6	10.6	8	9.1	3.1
2	3.5	8.7	9	9.5	2.7
3	5.2	7.0	10	10.0	2.2
4	6.3	5.9	12	10.7	1.5
5	7.2	5.0	14	11.3	0.9
6	7.9	4.3	40	12.2	0.0

[a] The acetonitrile vapor has been subtracted from these volumes. The barometric pressure was 705 mm.

Measurement of the Rate of Silver Chloride Deposition.—The 0.200 N solutions of silver nitrate and dimethylcarbamyl chloride in dry acetonitrile were thermostated at 38.90° and then a 5-ml. sample of each solution was pipetted into a flask immersed in the bath. After the proper time interval the flask was removed and the precipitated silver chloride filtered off, washed, dried and weighed. This procedure was followed for each point. The rates were then determined by the usual graphical treatment of the data.

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(15) The inverted Y-tube apparatus was designed by R. H. Boschan of this Laboratory.

(16) C. D. Hodgman, "Handbook of Chemistry and Physics," thirty-third Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1951, p. 1967.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

Synthesis of Some Epoxy Vinyl Monomers by Epoxidation with Peracetic Acid[1]

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A number of epoxy vinyl monomers—compounds which contain both a polymerizable double bond and an oxirane ring and which can be used in making cross-linked resins—were prepared by the peracetic acid epoxidation method. Studies of rates of epoxidation of several different types of double bonds with peracetic acid in various solvents were made to show the applicability of selective epoxidation.

The recent development of a process for the manufacture of peracetic acid in an inert solvent,[2] such as acetone or ethyl acetate, has allowed the preparation of many new types of epoxides. A particularly interesting class comprises those which contain both a reactive oxirane ring and a reactive double bond in the same molecule. These compounds, which we call epoxy vinyl monomers, are

(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Durham, N. C., November 17, 1957.

(2) B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, THIS JOURNAL, **79**, 5982 (1957); see also B. Phillips, P. S. Starcher, and B. D. Ash, *J. Org. Chem.*, **23**, 1823 (1958).