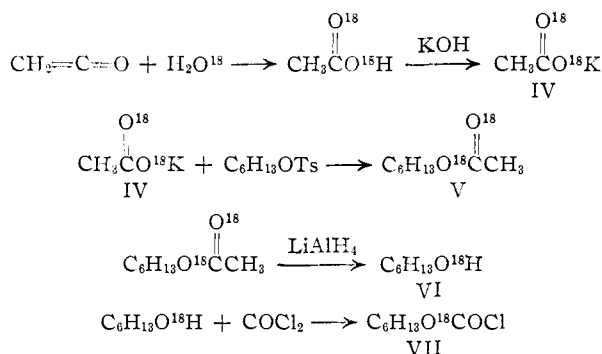
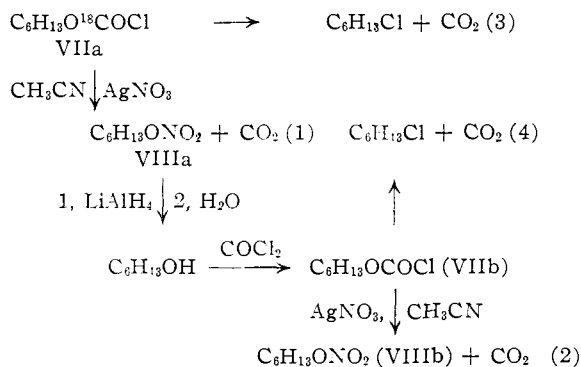


of studying its decomposition by silver nitrate in acetonitrile, *n*-hexyl chloroformate (VII), labeled with O^{18} in the oxygen atom adjacent to the alkyl group, was synthesized by the reaction sequence



Ketene⁴ was passed into water containing 1.4% H_2O^{18} to yield acetic acid containing, presumably, O^{18} in equal amounts on the carbonyl and hydroxyl oxygen atoms. Neutralization with potassium hydroxide produced potassium acetate (IV), which by reaction with *n*-hexyl *p*-toluenesulfonate yielded *n*-hexyl acetate (V). Reduction by lithium aluminum hydride gave rise to *n*-hexyl alcohol (VI), which was converted into *n*-hexyl chloroformate (VII), labeled in the desired position, by reaction with phosgene.

The O^{18} enriched *n*-hexyl chloroformate (VIIa) was converted to nitrate ester VIIIa by the action of silver nitrate in acetonitrile; VIIIa was converted back to hexyl chloroformate (VIIb) as shown, and then VIIb was again converted to nitrate ester VIIIb and CO_2 with silver nitrate in acetonitrile.



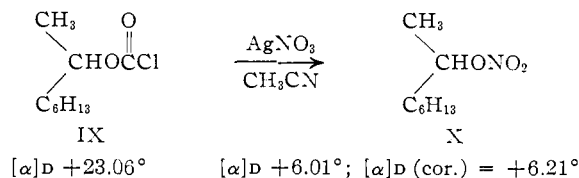
The ratios of the 46 and 44 peaks in the mass spectrometer for the CO_2 samples 1, 2, 3 and 4 were determined. The CO_2 samples (3) and (4) served to assay the different fractions of *n*-hexyl chloroformate and were obtained by the known⁵ decomposition of hexyl chloroformate in pyridine.

Formulas have been derived (see appendix) to calculate x , the fraction of the O^{18} in the original chloroformate ester that ends up attached to the alkyl group in the nitrate ester product. By this means, it can be shown that about 75% of the C–O bond in the hexyl chloroformate remains intact in going to nitrate ester.

(4) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, second edition, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 330.

(5) P. Carre, *Bull. soc. chim.*, [5] **3**, 1064 (1936).

(2) **Stereochemical Studies.**—Inasmuch as some cleavage of the C–O bond in hexyl chloroformate was found to occur upon its conversion to nitrate ester with silver nitrate in acetonitrile, it seemed pertinent to determine whether this cleavage is accompanied by retention or inversion of configuration at the α -carbon atom. Toward this end, optically active 2-octanol was converted to the chloroformate IX and then to the nitrate X by reaction with silver nitrate in acetonitrile.



The reported⁶ value of $[\alpha]_D$ for 2-octyl chloroformate is $+23.78^\circ$. If this value is taken to represent optically pure material, then the chloroformate IX used in this work is 96.9% optically pure. Accordingly, the "corrected" value of $[\alpha]_D$ for X is the rotation of X which presumably would have been observed had optically pure IX been used. The two reported^{7,8} values for $[\alpha]_D$ for X are 14.59° and 17.64° . With the higher of these two values, one can calculate an optical purity of 35.2% for X, corresponding to 67.6% retention and 32.4% inversion. Admittedly the polarimetric results can be interpreted in terms of 35% retention accompanied by racemization. However, in view of the fact that VIIa is converted to VIIIa leaving the C–O bond predominantly intact, the interpretation involving 70% retention and 30% inversion is favored.

Kinetic Studies.—A brief kinetic study of the reaction between *n*-hexyl chloroformate and silver nitrate in acetonitrile was indicative, although the results were not conclusive, of the fact that the rate of this reaction is approximately second-order or first-order in each of the reactants. These kinetic results were obtained by measuring the rate of evolution of carbon dioxide from the system. The small curvature of the second-order plot (see Fig. 1) is very likely due to the fact that an unstable intermediate is formed (see Discussion section) and that this intermediate decomposes by a first-order process, thus giving rise to complex kinetics in which a second-order process and a first-order process occur simultaneously. It is interesting that the rate of precipitation of silver chloride is slow here compared to that observed in the carbamyl chloride–silver nitrate reaction in which silver chloride is precipitated very rapidly.

Discussion

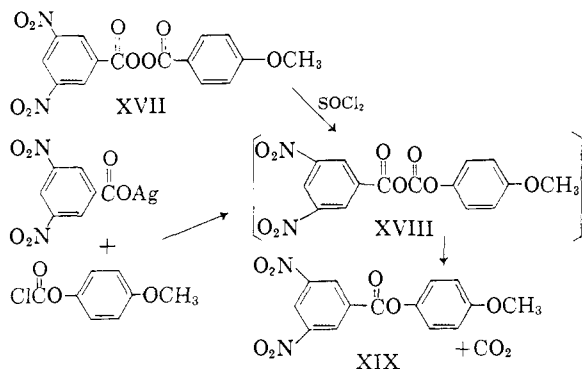
The experiments described herein strongly indicate that the conversion of an alkyl chloroformate to the corresponding nitrate proceeds mainly without rupture of the R–O bond in ROCOCl . It seems quite reasonable to assume some sort of intramolecular cyclic mechanism as shown here analogous to the "S_Ni" mechanism of the English

(6) H. Hunter, *J. Chem. Soc.*, **125**, 1389 (1924).

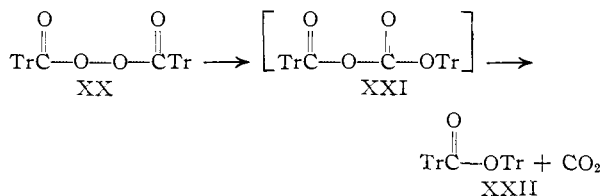
(7) R. L. Shriner and E. A. Parker, *THIS JOURNAL*, **55**, 766 (1933).

(8) S. J. Cristol, B. Franzus and A. Shadan, *ibid.*, **77**, 2512 (1955).

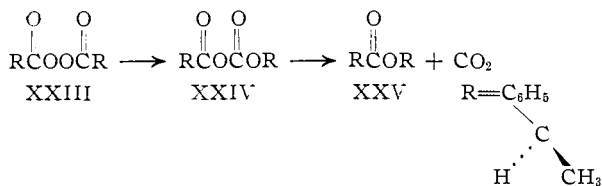
carboxylate esters. Leffler^{11,12} has isolated anisyl 3,5-dinitrobenzoate (XIX) from two reactions which very likely proceed *via* the intermediate anisyl 3,5-dinitrobenzoyloxycarbonate (XVIII) namely the decomposition of anisyl 3,5-dinitrobenzoyl peroxide (XVII) with thionyl chloride and the reaction of silver 3,5-dinitrobenzoate with anisyl chloroformate.



Bartlett and Green¹³ postulate a similar rearrangement for the conversion of ditriptyl peroxide (XX) to triptyloxy triptycyl carbonate (XXI). Inasmuch as triptycyl triptoate (XXII) is a product of the decomposition of XX, it seems quite possible that the origin of this ester could be *via* the intramolecular decomposition shown.



Similarly, intramolecular decomposition of the intermediate XXIV, postulated by Greene¹⁴ in the decomposition of hydratropyl peroxide (XXIII), is a likely mechanism for the formation of hydratropyl hydratropoate (XXV) with nearly complete retention of configuration.



Experimental

Hexyl Nitrate (Heterogeneous Medium).—A mixture of 20 g. (0.121 mole) of *n*-hexyl chloroformate (Eastman Kodak Co. white label), 30 g. (0.177 mole) of powdered silver nitrate and 50 ml. of carbon tetrachloride was refluxed until a sample of the solution gave a negative test when heated with alcoholic silver nitrate. During the reflux period, two 10-g. portions of powdered AgNO_3 were added to the solution. The total reflux time was two days. After filtering off the silver salts and removing the solvent at reduced pressure, the residue was distilled to yield two fractions of hexyl nitrate: I, b.p. 50–60° (8.3 mm.), n_D^{25} 1.4218,

1.66 g.; and II, b.p. 61–66° (8.2 mm.), n_D^{25} 1.4178, 5.48 g. The total yield of hexyl nitrate was 7.14 g. (40%); reported¹⁵ for *n*-hexyl nitrate, n_D^{25} 1.4180.

Hexyl Nitrate (Homogeneous Medium).—To a solution of 25 g. (0.147 mole) of silver nitrate in 75 ml. of acetonitrile was added 20.73 g. (0.126 mole) of *n*-hexyl chloroformate, and the solution was allowed to stand four days at room temperature, at which time an aliquot of the solution gave a negative test when heated with alcoholic silver nitrate. The solution was poured into 300 ml. of water and extracted with three 100-ml. portions of ether. Work-up of the ether extracts yielded 11.98 g. (64.8%) of *n*-hexyl nitrate, b.p. 55–58° (5.6 mm.), n_D^{25} 1.4180.

The infrared spectra on the hexyl nitrate samples showed the characteristic nitrate ester bands at 6.1 and 7.8 μ , and the absence of any hydroxyl or carbonyl absorption.

Cholesteryl Chloroformate.—Cholesteryl chloroformate, m.p. 118°, was prepared according to directions in the literature.¹⁶ The infrared spectrum of this material showed a strong carbonyl absorption band at *ca.* 5.6 μ and no hydroxyl band.

Reaction of Cholesteryl Chloroformate with Silver Nitrate. Preparation of Cholesteryl Nitrate.—To a solution of 3.0 g. (0.00668 mole) of cholesteryl chloroformate in 25 ml. of reagent grade benzene was added 3.0 g. (0.0176 mole) of powdered silver nitrate and the solution was refluxed. After two hours a sample of the solution gave a very small precipitate when heated with alcoholic silver nitrate. Powdered silver nitrate, 1.0 g., was added and refluxing was continued for another hour, at which time the alcoholic silver nitrate test was negative. After filtration of the silver salts and evaporation of the solvent, the residue crystallized readily to yield 2.63 g. (91.5%) of material. After one recrystallization from acetone there was obtained 2.14 g. (74.5% yield) of white needles, m.p. 115° (softens 110°). An analytical sample melting sharply at 115° was obtained after several more recrystallizations from acetone. The infrared spectrum showed the characteristic nitrate ester peaks at 6.1 and 7.8 μ and absence of carbonyl and hydroxyl peaks.

Anal. Calcd. for $\text{C}_{27}\text{H}_{45}\text{NO}_3$: C, 75.13; H, 10.51; N, 3.25. Found: C, 75.38, 75.31; H, 10.52, 10.77; N, 3.46, 3.54.

Saponification of Cholesteryl Nitrate.—A mixture of 1.0 g. (0.00232 mole) of cholesteryl nitrate, 4 pellets (0.59 g., 0.015 mole) of sodium hydroxide and 25 ml. of ethanol were sealed in a heavy-walled glass ampoule and heated overnight in the steam-bath. When the mixture was heated, all the solids dissolved and the solution soon became yellow. The ampoule was cooled and opened, and the contents were cooled in ice. A precipitate formed which was filtered off, m.p. *ca.* 139° after one recrystallization from 95% ethanol, m.p. 147–147.5° after a second recrystallization from 95% ethanol. The infrared spectrum of this material was identical with that of cholesterol.

Bornyl and cetyl chloroformates were prepared in good yield by passing phosgene into ethereal solutions of borneol and cetyl alcohol, respectively. Bornyl chloroformate, n_D^{25} 1.4740, was distilled at 78–81° (3.5 mm.), and cetyl chloroformate, n_D^{25} 1.4463, was distilled at less than 1 μ pressure at 100° in a Hickman molecular still.

Bornyl Nitrate.—Ten grams (0.0462 mole) of bornyl chloroformate and 15 g. (0.0883 mole) of powdered silver nitrate were dissolved in 30 ml. of dry acetonitrile. The mixture was allowed to stand at room temperature for 4 hours, during which time a quantity of silver chloride precipitated out. At the end of this time the solution gave a negative test for Cl with alcoholic silver nitrate. After filtering the silver salts and working up the solution, the bornyl nitrate was obtained by distillation at 58° (1.2 mm.), n_D^{25} 1.4768, in low yield.

Cetyl Nitrate.—To a solution of 15 g. (0.0492 mole) of cetyl chloroformate in 100 cc. of benzene was added 20 g. (0.118 mole) of powdered silver nitrate. The solution was refluxed for two days, after which the alcoholic AgNO_3 test was negative. The silver salts were filtered and the non-volatile residue, after removal of solvent, was distilled at less than 1 μ pressure on a Hickman molecular still at 100°.

(11) J. E. Leffler, private communication.

(12) J. E. Leffler, *THIS JOURNAL*, **72**, 67 (1950).

(13) P. D. Bartlett and F. D. Greene, *ibid.*, **76**, 1088 (1954).

(14) F. D. Greene, *ibid.*, **77**, 4869 (1955).

(15) L. M. Soffer, E. W. Parrotta and J. DiDomenico, *ibid.*, **74**, 5301 (1952).

(16) V. F. Kucherov and K. A. Kochesnikov, *J. Gen. Chem. (U.S.S.R.)*, **16**, 1137 (1946) (*C. A.*, **41**, 2703c (1947)).

The cetyl nitrate amounted to 11.78 g. (83.3%), n_{25}^D 1.4498.

Anal. Calcd. for $C_{18}H_{33}NO_3$: N, 4.87. Found: N, 4.73, 4.69.

O^{18} -Enriched Acetic Acid.—Into 200 g. (11.1 moles) of water enriched in O^{18} (1.4% enrichment from Stuart Oxygen Co.) was passed a slow stream of ketene (from a ketene generator) for 3 days. The reaction mixture was then distilled through 2 feet of glass helices. After the acetone fraction (distilled from the ketene generator) was removed, 80 g. of water, b.p. 98–99° (705 mm.), was recovered. The main acetic acid fraction, b.p. 113.9–114.0° (705 mm.), 321.3 g. (80% after correcting for recovered water), was collected.

O^{18} -Enriched Potassium Acetate.— O^{18} -Enriched acetic acid (100 g., 1.67 moles) was added in small portions to a cooled solution of 110 g. (1.67 moles) of 85% potassium hydroxide in 200 ml. of water. The solution was just neutralized by adding a few drops of O^{18} -enriched acetic acid and then freeze-dried overnight.

***n*-Hexyl *p*-Toluenesulfonate.**—*n*-Hexyl *p*-toluenesulfonate was prepared as described¹⁷ in the literature. The product was distilled through a Hickman molecular still at a pressure of *ca.* 1 μ . From 102 g. (1 mole) of redistilled 1-hexanol was obtained 230.0 g. (90%) of *n*-hexyl *p*-toluenesulfonate, n_{25}^D 1.4971 (reported¹⁷ n_{25}^D 1.4996).

O^{18} -Enriched *n*-Hexyl Acetate.—A mixture of 192 g. (0.75 mole) of *n*-hexyl *p*-toluenesulfonate, 100 g. (1.02 moles) of O^{18} -enriched potassium acetate, and 500 ml. of anhydrous ethanol was heated to reflux temperature. Within a few minutes, a copious quantity of precipitate (potassium *p*-toluenesulfonate) appeared. The mixture was allowed to reflux overnight. The solution was cooled and the precipitate was filtered to yield 150.4 g. (95.5%) of potassium *p*-toluenesulfonate, and the precipitate was washed with ether. Most of the ethanol was removed from the filtrate by distillation at aspirator pressure. Ether was added to the residue, and the resultant precipitate (potassium acetate plus potassium tosylate) was dissolved by addition of water and the layers separated. After drying, the ether extract was distilled to yield 76.9 g. (71%) of *n*-hexyl acetate, b.p. 164–167° (703.4 mm.), n_{25}^D 1.4068.

O^{18} -Enriched *n*-Hexyl Alcohol.—In a 2-liter 3-necked flask equipped with stirrer, reflux condenser and dropping funnel was placed a solution of 13 g. (0.34 mole) of finely powdered lithium aluminum hydride (Metal Hydrides, Inc.) in 600 ml. of anhydrous ether. The solution was cooled to –20 to –30° and a solution of 76.3 g. (0.53 mole) of O^{18} -enriched *n*-hexyl acetate in 300 ml. of ether was slowly added dropwise. Addition required *ca.* 3 hours. At no time during the addition did the temperature rise above –25°. After the addition the mixture was allowed to warm to room temperature and stir overnight. The excess lithium aluminum hydride and the salts were carefully decomposed with water and the mixture was extracted with ether and the ether extracts dried and distilled through a double center rod column to give the hexanol fraction, b.p. 154.5–155° (701.7 mm.), 45.5 g. (84%), n_{25}^D 1.4161; reported¹⁸ n_{25}^D 1.4179 for 1-hexanol.

O^{18} -Enriched *n*-Hexyl Chloroformate.—Into a solution of 40 g. (0.392 mole) of O^{18} -enriched *n*-hexyl alcohol in 30 cc. of anhydrous ether was passed a slow stream of phosgene for 5 hours. The excess ether was removed and the residue distilled at reduced pressure to yield 59.3 g. (92.2%) of *n*-hexyl chloroformate, b.p. 60° (7 mm.), n_{25}^D 1.4218.

Reaction of O^{18} -Enriched *n*-Hexyl Chloroformate with Silver Nitrate.—A solution of 17 g. (0.103 mole) of O^{18} -labeled hexyl chloroformate and 20 g. (0.117 mole) of silver nitrate in 50 cc. of acetonitrile (dried over CaH_2) was allowed to stand at room temperature. Part of the CO_2 evolved was collected and submitted for mass spectroscopic analysis. After several days time a negative chloride test resulted when a small aliquot of the solution was boiled with alcoholic silver nitrate. The silver chloride was filtered off, and the filtrate was poured into water and extracted with ether. Workup of the ether extract yielded 10.62 g. (70%) of *n*-hexyl nitrate, b.p. 56° (6 mm.).

Reduction of *n*-Hexyl Nitrate.—To a solution of 10 g. (0.26 mole) of lithium aluminum hydride in 300 ml. of dry ether was added dropwise with cooling a solution of 9.0 g. (0.068 mole) of hexyl nitrate in 100 ml. of anhydrous ether.

(17) F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 460 (1951).

(18) "Handbook of Chemistry and Physics," 37th edition 1955–1956, Chemical Rubber Publishing Co., Cleveland, Ohio.

The mixture was gradually allowed to warm to room temperature and kept under control by intermittent cooling. After no further vigorous reaction occurred (*ca.* 2 hours) the mixture was refluxed 4 hours. The workup was essentially the same as in the reduction of *n*-hexyl acetate and yielded 5.24 g. (84%) of 1-hexanol, b.p. 155–160°, n_{25}^D 1.4156.

2-Octyl Chloroformate.—Into a solution of 42.2 g. (0.323 mole) of *l*-2-octanol, $[\alpha]_D -8.55^\circ$, in 300 ml. of anhydrous ether was passed a slow stream of phosgene for 4 hours and the solution allowed to stand overnight. Removal of the ether and distillation of the residue yielded 58.3 g. (93%) of 2-octyl chloroformate, $[\alpha]_D -22.38^\circ$, b.p. 61° (2 mm.), n_{25}^D 1.4251; reported⁵ b.p. 92° (13 mm.), n_{25}^D 1.4282, $[\alpha]_D$ 23.78°. *d*-2-Octyl chloroformate, b.p. 61–63° (2.2 mm.), $[\alpha]_D$ 23.06°, was prepared in the same fashion from *d*-2-octanol, $[\alpha]_D$ 9.40°.

Reaction of *d*-2-Octyl Chloroformate with Silver Nitrate in Acetonitrile.—To a solution of 12.58 g. (0.0657 mole) of *d*-2-octyl chloroformate in 30 ml. of dry acetonitrile was added a solution of 14 g. (0.082 mole) of silver nitrate in 30 ml. of acetonitrile. The mixture was allowed to stand at room temperature for 4 days, at which time a small aliquot of the solution gave a negative chloride test with alcoholic silver nitrate. The workup was the same as in the hexyl chloroformate–silver nitrate runs. The octyl nitrate fraction amounted to 3.8 g. (30%), b.p. 50–60° (2 mm.), n_{25}^D 1.4251, $[\alpha]_D +6.01^\circ$; reported⁷ b.p. 55–56° (2 mm.), $[\alpha]_D$ 17.64°, n_{25}^D 1.4253. 2-Octanol, 2-octyl chloroformate and 2-octyl nitrate having the same sign of rotation have all been shown to have the same configuration.^{6–8}

Cholesteryl Trifluoroacetate.—To a solution of 1.00 g. (0.00453 mole) of silver trifluoroacetate in 10 ml. of anhydrous ether was added a solution of 2.00 g. (0.00445 mole) of cholesteryl chloroformate in 15 ml. of ether. There was no initial precipitate, but silver chloride formed slowly. After a day a small aliquot of the solution gave a negative test for chloride with hot alcoholic silver nitrate. The silver chloride was filtered off and the ether was evaporated to leave a white solid, m.p. 128–130° after one recrystallization from acetone. The yield after one recrystallization was 0.83 g. (77%). The analytical sample was recrystallized an additional five times from acetone and dried *in vacuo* over P_2O_5 ; m.p. 131–132°.

Anal. Calcd. for $C_{29}H_{45}O_2F_3$: C, 72.16; H, 9.40; F, 11.81. Found: C, 71.86; H, 9.27; F, 12.08.

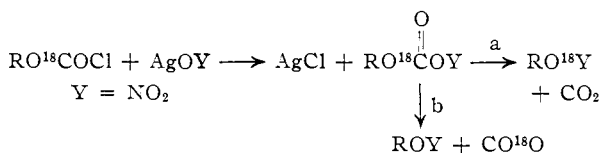
Kinetic Studies.—The rate of evolution of carbon dioxide from a solution containing 0.01 mole each of *n*-hexyl chloroformate and silver nitrate in a total of 10.0 cc. of redistilled acetonitrile was studied as described by Norris² in the kinetic study of the carbamyl chloride–silver nitrate reaction.

Mass Spectral Data.—The spectra of the carbon dioxide samples and of the O^{18} -labeled water and acetic acid samples were obtained with a Consolidated Engineering Corporation model 21-103 analytical mass spectrometer. The liquid samples were introduced into the sample system through a mercury orifice liquid introduction system, and the gas samples were introduced through the stainless steel inlet block.

Polarimetric Data.—All of the optical rotations were measured on an O.C. Rudolph and Sons Universal high precision polarimeter at 24°, the constant ambient temperature of the air-conditioned laboratory, in a 4-decimeter tube. The densities used were those reported in the literature.

Appendix

Derivation of Formulas Used in Treatment of O^{18} Data.—The reaction under consideration is



f_1 = fraction O^{18} in alkyl oxygen of $ROCOCl$

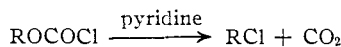
f_n = fraction O^{18} in normal oxygen

x = fraction of decomposition of $ROCOY$ by path a

$(1 - x)$ = fraction of decomposition of $ROCOY$ by path b

$$\begin{aligned}
 \text{gram-atoms O}^{18} \text{ in ROY} &= f_1x + f_n(1-x) \\
 \text{gram-atoms O}^{18} \text{ in CO}_2 &= 2f_nx + f_1(1-x) + f_n(1-x) = \\
 &= f_nx + f_1 + f_n - f_1x \\
 \text{Total gram atoms O}^{18} &= 2f_n + f_1 \\
 \text{gram-atoms O}^{16} \text{ in ROY} &= x(1-f_1) + (1-x)(1-f_n) \\
 \text{gram-atoms O}^{16} \text{ in CO}_2 &= 2x(1-f_n) + (1-x)(1-f_1) + \\
 &= (1-x)(1-f_n) \\
 \text{total gram-atoms O}^{16} &= 3 - 2f_n - f_1 \\
 \text{g.a. O}^{18} \text{ in ROY} &= f_1' = f_1x + f_n(1-x) \quad (2) \\
 \text{moles CO}_2^{46} &= \text{gram-atoms O}^{18} \text{ in CO}_2 = f_nx + f_1 + f_n - f_1x \\
 \text{moles CO}_2^{44} &= \text{total moles CO}_2 - \text{moles O}^{18} \\
 &= \frac{\text{total gram-atoms O in CO}_2 - \text{g.a. O}^{18} \text{ in CO}_2}{2} \\
 &= \frac{\text{g.a. O}^{16} \text{ in CO}_2 - \text{g.a. O}^{18} \text{ in CO}_2}{2} \\
 \frac{\text{moles CO}_2^{46}}{\text{moles CO}_2^{44}} &= \frac{46}{44} \text{ peak ratio in mass spectrometer} = \\
 &= \frac{2 \text{ g.a. O}^{18}}{\text{g.a. O}^{16} - \text{g.a. O}^{18}} = \frac{f_nx + f_1 + f_n - f_1x}{1 - f_1 + f_1x - f_nx - f_n} \quad (1)
 \end{aligned}$$

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



$$\begin{aligned}
 \text{g.a. O}^{18} &= f_1 + f_n \\
 \text{g.a. O}^{16} &= 2 - f_1 - f_n
 \end{aligned}$$

$$\begin{aligned}
 \text{no. of moles CO}_2^{46} &= \text{g.a. O}^{18} = f_1 + f_n \\
 \text{no. of moles CO}_2^{44} &= 1 - f_1 - f_n \\
 R_1 &= \frac{f_1 + f_n}{1 - f_1 - f_n} \quad (3)
 \end{aligned}$$

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]

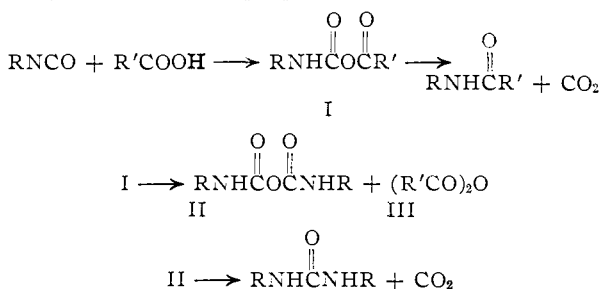
The Reaction of Dialkylcarbamyl Chlorides with Silver Nitrate¹

BY WILLIAM P. NORRIS

RECEIVED JUNE 16, 1958

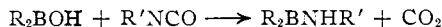
Dialkylcarbamyl chlorides react with silver nitrate to give the corresponding dialkylnitramines and dialkylnitrosamines plus carbon dioxide and other products. Silver nitrite and dimethylcarbamyl chloride give dimethylnitrosamine plus carbon dioxide and other products. The reactions presumably proceed 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 an-



hydrides 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 $\text{NCCCH}_2\text{COOH}$,

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



It is suggested that the above reactions all proceed through an unstable intermediate, of the

general formula $\text{RR}'\text{NCOX}$ (IV), where R =

alkyl or aryl, $\text{R}' = \text{H}$ and $\text{X} = \text{CR}$, SO_3H and $\text{B}(\text{OR})_2$. The present work extends the reaction to systems where R and $\text{R}' = \text{alkyl}$ and $\text{X} = \text{NO}_2$ or NO , affords a new synthetic route to dialkylnitramines and nitrosamines, and at the same time

(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. Verbanck, *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).