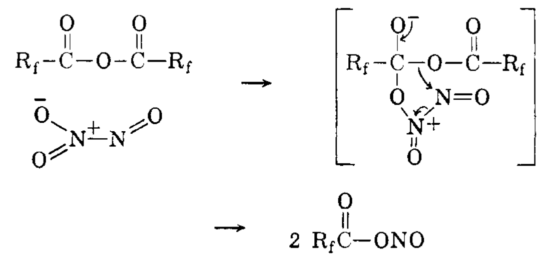

(3)

on the activated carbonyl carbon atom of the acid anhydride (equation 3).

Experimental

Materials.—The perfluoro acid anhydrides were prepared from reaction of the corresponding perfluoro acids with phosphorus pentoxide.[5,6] Dinitrogen trioxide was obtained from the Matheson Co.

Preparation of Nitrosyl Trifluoroacetate.—Dinitrogen trioxide (10.5 g., 0.138 mole) was condensed into a 250-ml. flask at Dry Ice temperature. The flask then was fitted with an addition funnel and Dry Ice-cooled reflux condenser and placed in an ice–salt bath maintained at −10 to −5°. Trifluoroacetic anhydride (28.7 g., 0.138 mole) was added to the flask through the addition funnel over a period of 5 min. After 30 min. the contents of the flask had become amber in color. Distillation of the material yielded 36.5 g. (92% yield) of nitrosyl trifluoroacetate, b.p. 45° at 80 mm. The infrared and n.m.r. spectra of the compound were identical with those of a sample prepared from silver trifluoroacetate and nitrosyl chloride.[1]

Preparation of Nitrosyl Perfluorobutyrate.—Dinitrogen trioxide (5.2 g., 0.068 mole) was condensed into a 30-cc. ampoule, cooled to liquid air temperature, and perfluorobutyric anhydride (28.0 g., 0.068 mole) was added. The ampoule was sealed under vacuum at liquid air temperature and then allowed to warm to room temperature over a period of 1 hr. Distillation of the product at reduced pressure yielded 31.5 g. (95% yield) nitrosyl perfluorobutyrate, b.p. 52° at 25 mm. The infrared and n.m.r. spectra of the compound were identical to those of a sample prepared from lead perfluorobutyrate and nitrosyl chloride.[1]

Preparation of Dinitrosyl Perfluorosuccinate.—Dinitrogen trioxide (15 g., 0.197 mole) was condensed into a 250-ml. flask cooled by Dry Ice and fitted with a Dry Ice-cooled reflux condenser. Perfluorosuccinic anhydride (16.0 g., 0.093 mole) was then added and the flask was warmed to 0° by means of an ice bath. After 15 min., the ice bath was removed and the flask was kept at room temperature for 30 min. Excess dinitrogen trioxide was removed at reduced pressure (1 mm.) at room temperature yielding 21.0 g. (91% yield) of dinitrosyl perfluorosuccinate, a yellow crystalline material, m.p. 44–48°. Heating the compound to its melting point or higher in a nitrogen atmosphere or at reduced pressure resulted in decomposition to perfluorosuccinic anhydride and dinitrogen trioxide. This decomposition also occurred, although much more slowly, at room temperature unless the compound was kept in a sealed tube. This apparent equilibrium results in the loss of small amounts of dinitrogen trioxide (and formation of small amounts of perfluorosuccinic anhydride) when handling the compound and is responsible for the somewhat high fluorine and low nitrogen values obtained.

Anal. Calculated for $C_4F_4N_2O_6$: C, 19.4; F, 30.7; N, 11.3. Found: C, 19.6; F, 31.7; N, 10.5.

A single n.m.r. peak at $C_6H_5{}^{*7} = 126.0$ was obtained in conformity with the proposed structure.

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Reactions of Tetrahalomethanes with Potassium *t*-Butoxide and Potassium Amide[1]

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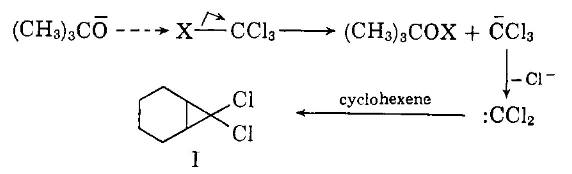
It has long been known that one of the halogen atoms of a tetrahalomethane is removed as positive halogen by an alkali hydroxide or alkoxide resulting in the formation of the corresponding haloform. Thus treatment of carbon tetrabromide and carbon tetraiodide with molecular equivalents of an alkali metal ethoxide in ethanol has afforded bromoform and iodoform, respectively.[2] Similar treatment of carbontetrachloride appeared to yield chloroform, but this haloform was not isolated.[2] More recently[3] iodotrifluoromethane was shown to react at room temperatures with potassium hydroxide in ethanol or 70% acetone to give fluoroform and potassium hypoiodite. Such reactions appear to involve displacements on halogen to form the hypohalite and trihalocarbanion, which acquires a proton from the medium. For example, the last reaction may be represented by equation 1.

$$\mathrm{HO^{-}} \dashrightarrow \mathrm{I}\overset{\curvearrowright}{—}\mathrm{CF_3} \longrightarrow \mathrm{HOI} + \mathrm{CF_3^{-}} \longrightarrow \mathrm{OI^{-}} + \mathrm{HCF_3} \qquad (1)$$

We have obtained evidence for the formation of the trihalocarbanion in the similar reactions of carbon tetrachloride and bromotrichloromethane with potassium *t*-butoxide in cyclohexene and tetrahydrofuran. Thus dichlorocarbene, which is a decomposition product of the trichlorocarbanion, was isolated as its cyclohexene adduct I in yields of 11–18% (Scheme A). The reaction mixture gave a positive test with starch-iodide in acetic acid indicating the presence of *t*-butyl hypohalite, though this product was not isolated. Hypohalites are known to react with olefins.[4]



Scheme A

Somewhat similarly, Watt and co-workers[5] have observed that one of the iodine atoms of carbon tetraiodide is more reactive than the other three towards potassium amide in liquid ammonia, and that a total of five molecular equivalents of this reagent are neutralized by one of the tetrahalide. They assumed that the initial products were iodoamine and iodoform, and that potassium amide converted the former compound to hydrazine and the latter to cyanide ion. Hydra-

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(5) R. F. Clark and J. H. Simons, *J. Am. Chem. Soc.*, **75**, 6305 (1953).

(6) A. L. Henne and S. B. Richter, *ibid.*, **74**, 5420 (1952).

(7) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

(1) Supported by the National Science Foundation.

(2) J. U. Nef, *Ann.*, **308**, 329 (1899).

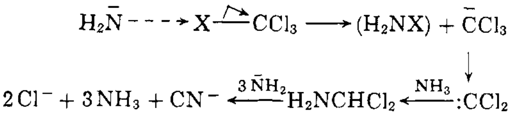
(3) J. Banus, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, **60**, (1951).

(4) C. F. Irwin and G. F. Hennion, *J. Am. Chem. Soc.*, **63**, 858 (1941).

(5) G. W. Watt, W. R. McBride, and D. M. Sowards, *ibid.*, **78**, 1562 (1956).

zine was shown to react with carbon tetraiodide to give nitrogen and iodoform.

We have observed that carbon tetrachloride and bromotrichloromethane react similarly with potassium amide in liquid ammonia to form cyanide ion, which, it is suggested, arises through the intermediate formation of dichlorocarbene (Scheme B).



$$H_2\bar{N} \dashrightarrow X\text{—}CCl_3 \longrightarrow (H_2NX) + \bar{C}Cl_3$$
$$2\,Cl^- + 3\,NH_3 + CN^- \xleftarrow{3\,\bar{N}H_2} H_2NCHCl_2 \xleftarrow{NH_3} :CCl_2$$

Scheme B

That dichlorocarbene was an intermediate was supported by the detection (by vapor phase chromatography) of a small amount (1%) of its cyclohexene adduct I when the reaction was carried out in the presence of cyclohexene. Better yields (17–26%) of I have recently been obtained in the corresponding reaction of tetrahalomethanes with potassium diphenylmethide.[6]

Similar to the observation of Watt[5] with carbon tetraiodide, the present reaction with carbon tetrachloride evidently involved five molecular equivalents of potassium amide. Thus, these proportions of reactants afforded cyanide ion in 94% yield, whereas the yield was only about one fifth this amount (19%) when molecular equivalents of reactants were employed. Similarly the reaction of bromotrichloromethane with two molecular equivalents of the reagent afforded cyanide ion in 38% yield. Although only four molecular equivalents of amide ion are indicated in Scheme B, a fifth equivalent of the reagent would presumably be neutralized in ionizing the monohaloamine, which is evidently a much stronger acid than ammonia.[7]

The fate of the monohaloamine, assumed to be formed in the initial displacement on halogen (see Scheme B) was not established. Evidently it was not converted appreciably to hydrazine as has been assumed for iodoamine,[5] since only a trace of benzalazine was detected on treatment of the reaction product with excess benzaldehyde. Although control experiments indicated that about 50% of the hydrazine would have been destroyed under the conditions employed,[8] the remaining 50% should have been detected. Moreover, treatment of potassium amide in liquid ammonia with an ethereal solution of chloroamine failed to afford an appreciable amount of hydrazine. Since the monohaloamine would presumably have been ionized by the amide ion (see above), the resulting anion ($\bar{N}HCl$) might have been converted to ammonia and nitrogen through the intermediate NH, as has been proposed previously.[9] No attempt was made in the present investigation to detect nitrogen.

Although chloroform may be in equilibrium with the trichloro carbanion (see Scheme B), an attempt to isolate it by adding a liquid ammonia solution of potassium amide to carbon tetrachloride was unsuccessful. This is not surprising since chloroform was shown to be converted rapidly to cyanide ion, which was obtained in 93% yield employing one molecular equivalent of chloroform to four of the reagent. Presumably the initial reaction involved abstraction of the proton from chloroform to form the trichloro carbanion, which underwent decomposition as shown in Scheme B.

Experimental

Reactions of Tetrahalomethanes with Potassium *t*-Butoxide.—Potassium *t*-butoxide was prepared by dissolving 3.3 g. (0.0875 g.-atom) of potassium in *t*-butyl alcohol, evaporating excess solvent and heating the residue to 110° at 1.6 mm. The resulting solid was added to 80 ml. of cold cyclohexene, and 13.3 g. (0.0875 mole) of carbon tetrachloride was added slowly. The mixture was stirred at room temperature for 7 hr., then at the boiling point for 2 hr. Cold water was added and the organic layer was separated, dried over sodium sulfate, and evaporated. The residual oil gave a positive test with starch–iodide reagent in acetic acid. Vapor phase chromatography of the oil showed the presence of a small amount of 7,7-dichloronorcarane, identified by comparison of its retention time with that of an authentic sample.

In another experiment, potassium *t*-butoxide was prepared from 4.75 g. (0.12 g.-atom) of potassium. To a suspension of the base in a chilled mixture of 40 ml. of cyclohexene and 80 ml. of tetrahydrofuran was added 25 g. (0.626 mole) of bromotrichloromethane in 20 ml. of tetrahydrofuran. The mixture was stirred overnight at 0°, then for 10 days at room temperature. Samples were withdrawn periodically for analysis by vapor phase chromatography, and the yield (3.6 g., 18%) of 7,7-dichloronorcarane appeared to be constant after 4 days. The chromatogram showed several other peaks. Three distillations afforded a sample, b.p. 80–82° at 15 mm., that had an infrared spectrum identical with authentic 7,7-dichloronorcarane.

Reaction of Carbon Tetrachloride with Potassium Amide.—To a stirred solution of 0.025 mole of potassium amide in 150 ml. of commercial, anhydrous liquid ammonia was added 0.77 g. (0.005 mole) of carbon tetrachloride in dry ether. After 10 min., the liquid ammonia was evaporated quickly (steam bath), and the residue dissolved in water. The yield of cyanide ion[10] was 0.0047 mole (94%) based on carbon tetrachloride. The aqueous solution was acidified with acetic acid, and benzaldehyde was added to test for hydrazine,[5] but no benzalazine was isolated.

In another experiment under the same conditions, 50 ml. of ethanol was added prior to the evaporation of the liquid ammonia. After filtering, the resulting ethanolic solution was treated with 1.4 g. (0.013 mole) of benzaldehyde and a small quantity of water. After 2 hr., an analysis of the solution by vapor phase chromatography indicated the presence of only a trace (<1%) of benzalazine. A blank experiment showed that hydrazine could be recovered from liquid ammonia as the benzalazine derivative in 82% yield using this procedure.

In a control experiment, a solution of 0.71 g. (0.0046 mole) of carbon tetrachloride and 0.15 g. (0.0046 mole) of hydrazine in dry ether was added to a stirred solution of 0.023 mole of potassium amide in 150 ml. of liquid ammonia. After 10 min., 50 ml. of ethanol was added, and the liquid ammonia was evaporated. There was recovered from the resulting ethanolic solution 48% of the hydrazine as benzalazine.

When a solution of 0.02 mole each of carbon tetrachloride and hydrazine in a small quantity of dry ether was added to 150 ml. of liquid ammonia, and the mixture stirred for 1.5 hr., there was recovered 46% of the hydrazine as benzalazine. Also chloroform was detected by vapor phase chromatography. Previously a refluxing mixture of carbon tetrachloride and hydrazine had been observed to afford chloroform and nitrogen.[11]

Reaction of Bromotrichloromethane with Potassium Amide.—Several experiments were performed in liquid ammonia affording results similar to those described above for carbon tetrachloride.

In one experiment, 0.1 mole of potassium amide was prepared in liquid ammonia, and the ammonia was replaced by 100 ml. of ether and 125 ml. of tetrahydrofuran. To the resulting stirred

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(6) C. R. Hauser, W. G. Kofron, W. R. Dunnavant, and W. F. Owens, *J. Org. Chem.*, **26**, 2627 (1961).

(7) The pK_a of monochloroamine has been estimated to be 15 ± 2; L. F. Audrieth, E. Colton, and M. M. Jones, *J. Am. Chem. Soc.*, **76**, 1428 (1954).

(8) Even in the absence of amide ion, hydrazine is slowly destroyed by carbon tetrachloride in liquid ammonia, but this need not be taken into account (see Experimental).

(9) L. F. Audrieth and R. A. Rowe, *J. Am. Chem. Soc.*, **77**, 4726 (1955).

(10) F. Charlot and D. Bezier, "Quantitative Inorganic Analysis," transl. by R. C. Murray, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 380.

(11) S. H. Patrinkin and E. Lieber, *J. Am. Chem. Soc.*, **72**, 2778 (1950).

suspension was added a solution of 9.93 g. (0.05 mole) of bromotrichloromethane in 50 ml. of cyclohexene. The suspension was stirred at room temperature for 60 hr. Ice was added, and the organic layer was separated and concentrated. The residual oil was shown by vapor phase chromatography to contain about 1% (based on the amount of bromotrichloromethane consumed) of 7,7-dichloronorcarane (I), identified by comparison of the retention time with that of an authentic sample. The aqueous solution did not give a Prussian blue test for cyanide ion. From the oil was recovered 6.36 g. (64%) of bromotrichloromethane. Some of this starting material was probably lost during the work-up.

Treatment of Chloroamine with Potassium Amide.—To a stirred solution of 0.05 mole of potassium amide in 150 ml. of liquid ammonia was added an ethereal solution of 0.018 mole of chloroamine.[12] The ammonia was allowed to evaporate and water was added. A portion of the aqueous solution was acidified with acetic acid, and benzaldehyde was added. The mixture developed a gray turbidity, but no weighable amount of solid was collected.

Reaction of Chloroform with Potassium Amide.—To a solution of 0.075 mole of potassium amide in 150 ml. of liquid ammonia was added an ethereal solution of 2.25 g. (0.019 mole) of chloroform. A vigorous reaction took place. The ammonia was evaporated, and the residue was dissolved in water. The yield of cyanide ion[10] was 0.017 mole (93%).

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(12) G. H. Coleman and C. R. Hauser, *J. Am. Chem. Soc.* **50**, 1193 (1928).

Action of Tertiary Amines and Phosphines upon Alkyl β-Bromopropionylcarbamates

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The recent report of Johnson and Schweitzer[1] concerning the dehydrobromination of alkyl or aryl β-bromopropionylcarbamates and ureas prompts us to disclose some similar results from a synthetic rather than a kinetic approach to the problem.

When β-bromopropionylcarbamates, made by the reaction of alcohols with β-bromopropionyl isocyanate,[2,3] are allowed to react with a variety of tertiary amines, the products (Table I) indicate that the reaction can proceed in two different ways (equations 1 and 2).

$$\begin{tikzcd}
 & R'_3\overset{+}{N}CH_2CH_2CONHCOOR,\ Br^- \quad (1) \\
BrCH_2CH_2CONHCOOR + R'_3N \arrow[ur] \arrow[dr] & \\
 & CH_2{=}CHCONHCOOR + R'_3N\cdot HBr \quad (2)
\end{tikzcd}$$

When R is *n*-octadecyl, dried pyridine leads to the quaternary salt (equation 1). Quaternization also takes place in pyridine which has not been specially dried, but under these conditions hydrolysis of the ester group also results (equation 3). With triphenylphosphine and tri-*n*-butylphosphine, the quaternization reaction

$$BrCH_2CH_2CONHCOOR + C_5H_5N \xrightarrow{H_2O} C_5N_5\overset{+}{N}CH_2CH_2CONH_2,\ Br^- + CO_2 + ROH \quad (3)$$

also takes place. However, in all other cases studied, the elimination reaction (equation 2) predominated as the reasonably high yield of products indicates. The reactions proceed in the same manner when R is ethyl or cholesteryl rather than octadecyl.

TABLE I

RESULTS OF REACTION OF ALKYL β-BROMOPROPIONYLCARBAMATES WITH TERTIARY AMINES AND PHOSPHINES

R	Base	Reaction	Quaternary salt	% Yield acrylylcarbamate	% Yield amine hydrobromide
C_2H_5	C_5H_5N	1	68		
n-$C_{18}H_{37}$	C_5H_5N[a]	1	62		
Cholesteryl	C_5H_5N	3	84[b]		
n-$C_{18}H_{37}$	C_5H_5N	3	76		
n-$C_{18}H_{37}$	$(C_6H_5)_3P$	1	60		
n-$C_{18}H_{37}$	$(n\text{-}C_4H_9)_3P$	1	42		
n-$C_{18}H_{37}$	$(C_2H_5)_3N$	2		84	95
n-$C_{18}H_{37}$	$(n\text{-}C_4H_9)_3N$	2		92	
n-$C_{18}H_{37}$	N-Ethylpiperidine	2		85	
n-$C_{18}H_{37}$	[c] (1 equiv.)	2			56 (di-HBr)
n-$C_{13}H_{37}$	[c] (2 equiv.)	2			42 (mono-HBr)
Cholesteryl	$(n\text{-}C_4H^9)_3N$	2		79	
C_2H_5	$(C_2H_5)_3N$	2		79	75

[a] Dried with and distilled from calcium hydride. [b] Cholesterol was also isolated in 68% yield. [c] 1,4-Diazabicyclo[2.2.2]octane.

The pK_a values of pyridine, tri-*n*-butylamine, and triethylamine are 5.23, 9.93, and 10.78.[4] The results indicate, therefore, that the course of reaction as well as the rate of the elimination reaction[1] is strongly dependent upon the base strength of the amine.

Treatment of octadecyl β-bromopropionylcarbamate with excess dry pyridine gave 1-(3,5-dioxo-6-oxa-4-azatetracosyl)pyridinium bromide in 62% yield. When the reaction was run in acetonitrile using only one equivalent of pyridine, a 74% yield of the quaternary bromide resulted. When pyridine hydrobromide and octadecyl acrylcarbamate were allowed to react in acetonitrile under identical conditions, a 62% yield of the quaternary bromide resulted. Owing to the small difference between these yields, we are unable to choose (as were Johnson and Schweitzer[1]) between displacement and elimination–addition mechanisms for the quaternization of the β-bromopropionylcarbamates.

Experimental[5]

Materials.—Sodium tetraphenylboron was obtained from K and K Laboratories, tri-*n*-butylphosphine from Westvaco Mineral Products Division of Food Machinery and Chemical Corp., hydrogen bromide from the Matheson Co., Inc., and 1,4-diazabicyclo[2.2.2]octane from Houdry Process Corp. All other materials were Eastman organic chemicals. "Dried" pyridine was refluxed for 2 hr. with and distilled from calcium hydride.

I. Quaternizations. 1-(3,5-Dioxo-6-oxa-4-azaoctyl)pyridinium Tetraphenylboride.—A solution of 5.00 g. (0.0223 mole) of ethyl β-bromopropionylcarbamate,[3] 1.77 g. (0.0223 mole) of pyridine, and 50 ml. of acetonitrile was refluxed for 15 hr., cooled

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(1) H. W. Johnson, Jr., and M. Schweitzer, *J. Org. Chem.*, **26**, 3666 (1961).

(2) J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, **79**, 2533 (1957); H. W. Johnson, Jr., and D. E. Bublitz, *ibid.*, **80**, 3150 (1958).

(3) H. W. Johnson, Jr., H. A. Kreyssler, and H. L. Needles, *J. Org. Chem.*, **25**, 279 (1960).

(4) M. Tamres, S. Searles, E. M. Leighly, and D. W. Mohrman, *J. Am. Chem. Soc.*, **76**, 3983 (1954).

(5) Melting points were determined on a Fisher–Johns apparatus, unless otherwise noted, and are corrected.