TABLE III

PREPARATION OF HYDRAZONES

Compound	M.p., °C.	Yield, %
Toluene-*p*-sulfonylhydrazones		
Benzaldehyde	155–158°	92
p-Methoxybenzaldehyde	112–114°	93
Acetophenone	147.5–150°	82
m-Nitroacetophenone	176.5–179°	93
Propiophenone	122–125°	96
Cyclohexanone	155–158°	67
Nortricyclenone	160–162°	74
Norcamphor	206.5–208°	89
o-Nitrobenzenesulfonylhydrazones		
Benzaldehyde	175–177°	65
Acetophenone	105–107°	60

pound (1 equivalent) and *o*-nitrobenzenesulfonylhydrazine[4] (1 equivalent) in cold acetic acid was digested on a hot plate for 5–10 min. The mixture was cooled to 5°, and the precipitated product was filtered, washed with cold acetic acid and water, and air dried. The yields and melting points of the *o*-nitrobenzenesulfonylhydrazones thus obtained are recorded in Table III.

Preparation of Diazoalkanes.—In general, a 10% solution of the hydrazone in fresh pyridine was mixed with the desired amount of the appropriate base. The mixture was then stirred in a water bath maintained at the desired temperature. Spectroscopic analysis was carried out by dilution of aliquots with ten times their volume of water, extraction of the diazoalkane into pentane, and dilution of the pentane extracts to volume with further pentane.

The following preparation of 1-phenyldiazopropane is illustrative of the procedure used on a preparative scale.

1-Phenyldiazopropane.—Propiophenone toluene-*p*-sulfonylhydrazone (1.0 g., 3.3 mmoles) and commercial sodium methoxide (180 mg., 3.3 mmoles) were mixed in fresh pyridine (10 ml.). The mixture was protected with a Drierite drying tube and heated with stirring for 1 hr. in a water bath held at 60–65°. The initial precipitate dissolved and a granular precipitate began to collect during this time, while the supernatant solution turned wine red. At the end of the heating period the mixture was poured into ice-water (50 ml.) and extracted with two 20-ml. portions of pentane. The combined pentane extracts were washed with four 25-ml. portions of cold water and once with saturated aqueous sodium chloride. The wine red organic solution was then dried over anhydrous sodium sulfate at 5°, filtered, and evaporated to dryness *in vacuo* at room temperature. The residual red oil (0.29 g.) liberated 1.8 mmoles of nitrogen (measured volumetrically and corrected to STP) when treated with acetic acid, corresponding to a yield of 55% and a purity of 90%.

Acknowledgment.—The author wishes to thank the Petroleum Research Fund for support of this work under grant PRF 742A4.

[4] A. T. Dann and W. Davies, *J. Chem. Soc.*, 1050 (1929).

The Preparation of Nitrosyl Perfluoroacylates from Perfluoro Acid Anhydrides and Dinitrogen Trioxide

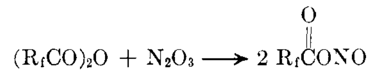
D. E. RICE AND G. H. CRAWFORD

Contribution No. 252, Central Research Laboratories, Minnesota Mining & Manufacturing Company, Saint Paul 19, Minnesota

Received November 19, 1962

Recent publications have described the preparation of nitrosyl perfluoroacylates from the reaction of metal salts of perfluoro acids with nitrosyl chloride[1,2] and from the reaction of perfluoro acid anhydrides with nitrosyl chloride.[3]

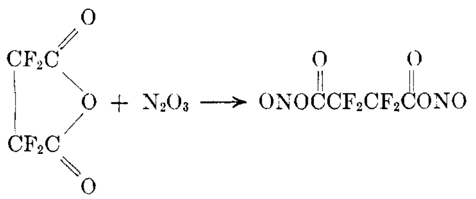
In the present investigation, it was found that nitrosyl perfluoroacylates can be prepared conveniently in high yields from the liquid phase reaction of perfluoro acid anhydrides with dinitrogen trioxide (equation 1).



$$(R_fCO)_2O + N_2O_3 \longrightarrow 2\ R_f\overset{\overset{O}{\|}}{C}ONO \qquad (1)$$

The reaction is carried out by simply mixing equimolar quantities of the two reactants or by titrating one reactant with the other. Since dinitrogen trioxide is deep blue and nitrosyl perfluoroacylates are amber or yellow, the course of the reaction can be followed by the color of the reaction mixture. The reaction can be carried out at atmospheric pressure, using a Dry Ice-cooled reflux condenser to maintain dinitrogen trioxide in the liquid phase or in a sealed vessel under autogeneous pressure. For the case of trifluoroacetic anhydride and dinitrogen trioxide, reaction is complete in approximately twenty minutes at −5° and in 3.5 minutes at 25°.

When cyclic perfluoro acid anhydrides are used in the reaction, dinitrosyl perfluoroacylates are produced. For example, perfluorosuccinic anhydride and dinitrogen trioxide reacted at 0° to give dinitrosyl perfluorosuccinate (equation 2).



(2)

This compound is highly reactive and exhibits the normal reactions of nitrosyl perfluoroacylates with water, alcohols, metals, etc.[1] Pyrolysis at temperatures of 50° and higher[4] gives only perfluorosuccinic anhydride and dinitrogen trioxide in contrast to the nitrosyl perfluoroacylates derived from straight chain perfluoro acid anhydrides which yield perfluoronitrosoalkanes upon pyrolysis.[1,2]

Evidence indicates that the reaction is quite general. It proceeds most readily with acid anhydrides which are activated by electron-withdrawing groups. For example, reaction at room temperature has been observed with trichloroacetic anhydride but not with acetic anhydride. The reaction of dinitrogen trioxide with nonfluorinated acid anhydrides will be reported at a later date.

The reaction conditions and electronic requirements of the reaction indicate that the reaction mechanism is ionic, involving an initial attack of the negatively charged oxygen atom of the dinitrogen trioxide molecule

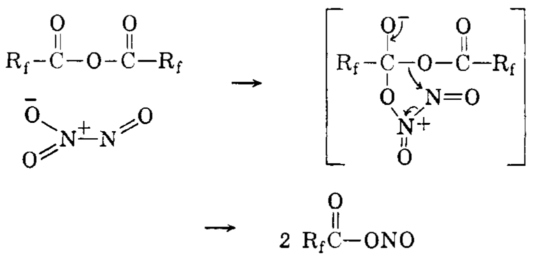
---

[1] C. W. Taylor, T. J. Brice, and R. L. Wear, *J. Org. Chem.*, **27**, 1064 (1962).

[2] R. E. Banks, R. N. Haszeldine, and M. K. McCreath, *Proc. Chem. Soc.*, 64 (1961).

[3] J. D. Park, R. W. Rosser, and J. R. Lacher, *J. Org. Chem.*, **27**, 1462 (1962).

[4] The explosion hazards associated with super heating nitrosyl perfluoroacylates have been described by Taylor, Brice and Wear (ref. 1).



(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.

Acknowledgment.—The authors wish to thank W. J. Fraser, C. W. Taylor, and D. R. Yarian for their assistance. This work was supported by contract DA-19-129-QM-1684 from the U. S. Army Quartermaster Corps.

---

(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).

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

William G. Kofron, Fred B. Kirby, and Charles R. Hauser

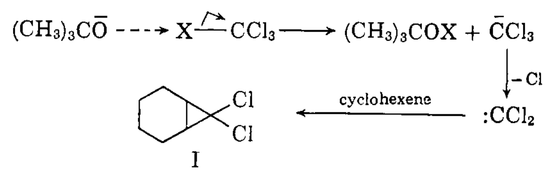
Department of Chemistry, Duke University, Durham, North Carolina

Received August 3, 1962

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.

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

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-

---

(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).