Methyl glycidyl ether was obtained by the method of Pollard.[5] The thiiranes were prepared from the corresponding epoxides following the procedure of Bordwell and Anderson.[6] Triethyl phosphite was obtained from the Virginia-Carolina Chemical Corporation and purified prior to use by distillation from metallic sodium.

Reaction of 2-chloromethylthiirane with triethyl phosphite. A mixture of 21.6 g. (0.20 mole) of 2-chloromethylthiirane and 33.2 g. (0.20 mole) of triethyl phosphite was distilled at atmospheric pressure employing a 30 cm. Fenske type column, removing distillate at such a rate that the distillate temperature remained in the range 45–46°. At the end of a 5 hr. period the temperature of the residual material remaining in the distillation flask had reached 180°. At this point 14.8 g. (0.195 mole) of allyl chloride had been obtained as distillate. Redistillation of the chloride gave 14.6 g. (0.190 mole), a 95% yield of allyl chloride, b.p. 44.8–45°/741.4 mm., n_D^{25} 1.4116. Literature values,[7] b.p. 44.7–44.8/760 mm., n_D^{25} 1.4116. Distillation of the liquid residue in the distillation flask under reduced pressure afforded 39.6 g. (0.20 mole) of triethyl thionophosphate distilling at 82–83°/5 mm., n_D^{25} 1.4460, n_D^{20} 1.4481. The reported[4,6] physical constants of thionophosphate are: b.p. 45°/0.5 mm., 105–106°/20 mm., n_D^{20} 1.4480, n_D^{25} 1.4461. Thus, a quantitative yield of triethyl thionophosphate was obtained. When the original distillation residue was heated above 180° or kept at about that temperature for long periods of time, the liquid became dark colored and subsequent distillation failed to give quantitative yields of triethyl thionophosphate. A possible explanation of this is found in the work of Emmett and Jones[8] who observed that thionophosphates readily undergo thermal isomerization to phosphorothiolates.

Reaction of 2-methylthiirane with triethyl phosphite. A mixture of 14.8 g. (0.20 mole) of 2-methylthiirane and 33.2 g. (0.20 mole) of triethyl phosphite was distilled employing the experimental procedure described above except that bromine-carbon tetrachloride traps were installed to collect any propylene liberated. At the end of 3 hr. of distillation the temperature of the residue had reached 180° at which point heating was discontinued. Vacuum distillation of the liquid residue gave 39.2 g. (0.199 mole) a 99% yield of triethyl thionophosphate. Treatment of the material in the bromine-carbon tetrachloride traps, following standard procedures, afforded a 97% yield of 1,2-dibromopropane, b.p. 137°/734.6 mm, n_D^{20} 1.5193. Literature[9] values for this dibromide are: b.p. 139°–142°, n_D^{20} 1.5194.

Reaction of 2-methoxymethyl thiirane[10] with triethyl phosphite. Distillation of a mixture containing 20.8 g. (0.20 mole) of 2-methoxythiirane and 33.2 g. (0.20 mole) of triethyl phosphite by experimental techniques already described gave a 94% yield of methyl allyl ether, b.p. 42°/746.5 mm, n_D^{20} 1.3786. The reported[11] physical constants for allyl ether are: b.p. 42.5–43°/757 mm, n_D^{25} 1.3778–1.3803. The other product in this reaction, triethyl thionophosphate, was obtained in a 96% yield.

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Nitration Studies. X. Reaction of Dinitrogen Tetroxide with Hydrazides and Isocyanates[1]

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In its reactions with organic compounds, dinitrogen tetroxide sometimes behaves like a pseudo halogen and sometimes like a mixed anhydride of nitrous and nitric acids. Thus it reacts with aliphatic hydrocarbons to produce nitro alkanes in much the same way that chlorine produces chloro alkanes. However it reacts with aromatic amines to produce diazonium salts in much the same way that nitrous acid does. In continuing our efforts to clarify its chemical behavior we have investigated the reaction of dinitrogen tetroxide with acid hydrazides.

Carpino[3] has recently shown that acid hydrazide hydrochlorides react with chlorine to give acid chlorides. However, much earlier Curtius[4] showed that acid hydrazides react with nitrous acid to form acid azides, then isocyanates, and finally the solvolysis or solvation products of isocyanates. We have found that ethanoyl hydrazide reacts with dinitrogen tetroxide in a 1:1 mole ratio to give methyl amine nitrate, nitrogen, carbon dioxide, and acetic acid. The methyl amine nitrate was obtained in a 56% yield; the nitrogen and carbon dioxide evolved corresponded to 100% and 40% respectively of the expected amounts. The amount of acetic acid isolated was small, about 10% of theory, and probably arose from partial hydrolysis of the hydrazide or the azide. The methyl amine nitrate was identified by comparison with an authentic synthetic sample and by conversion to sodium nitrate and to the phenyl isothiocyanate derivative of methyl amine.

Butanoyl hydrazide reacts with dinitrogen tetroxide in an approximately 1:1 mole ratio to give propyl amine nitrate in 54% yield together with nitrogen, carbon dioxide, and some butyric acid.

The above reactions are assumed to proceed according to the following equations.

$$(1)\quad RCONHNH_2 + N_2O_4 \longrightarrow RCON_3 + HNO_3 + H_2O$$

$$(2)\quad RCON_3 \longrightarrow RNCO + N_2$$

$$(3)\quad RNCO + H_2O \longrightarrow RNH_2 + CO_2$$

$$(4)\quad RNH_2 + HNO_3 \longrightarrow RNH_3NO_3$$

$$(5)\quad RCONHNH_2 + N_2O_4 \longrightarrow RNH_3NO_3 + CO_2 + N_2$$

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(1) From the M. S. thesis of W. Michalowicz, Purdue University, January 1958.

(2) Present address: Koppers Company, Inc., Pittsburgh, Pa.

(3) L. A. Carpino, *Chem. and Ind.* (*London*), 123 (1956).

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On mixing the reagents at ice bath temperatures, a vigorous reaction occurs. The resulting solution gives a positive test for azides. A steady evolution of gas develops and grows more vigorous as the temperature of the mixture is allowed to approach and exceed room temperature. This decomposition may be completed by warming the mixture on a water bath. The product remaining in the reaction flask is a solution of the amine nitrate in chloroform contaminated with a small amount of the corresponding carboxylic acid.

Since isocyanates are assumed to be intermediates in the above reaction, it was decided to investigate their behavior with dinitrogen tetroxide also. Phenyl isocyanate gives immediately a brown precipitate with liquid dinitrogen tetroxide. Upon complete evaporation of the excess liquid dinitrogen tetroxide the brown solid explodes violently. However phenyl isocyanate reacts smoothly with dinitrogen tetroxide in chloroform solution in a 1:1 mole ratio to yield benzene diazonium nitrate in 56% yield. The carbon dioxide evolved corresponds to 76% of the expected amount. The benzene diazonium nitrate decomposes slowly if left in the chloroform solution to form a tar from which *o*-nitrophenol may be isolated.

$$(6)\ C_6H_5NCO + N_2O_4 \longrightarrow C_6H_5N_2NO_3 + CO_2$$

$$(7)\ C_6H_5N_2NO_3 \longrightarrow N_2 + o\text{-}HOC_6H_4NO_2$$

Ethyl isocyanate reacts with dinitrogen tetroxide in chloroform solution in a 1:1 mole ratio to give ethyl nitrate, carbon dioxide, nitrogen and traces of ethylene and nitric acid. Since ethyl isocyanate reacts with dinitrogen tetroxide under anhydrous conditions to give ethyl nitrate instead of ethyl amine nitrate, it must be presumed that the formation of amine nitrates by reaction of acid hydrazides with dinitrogen tetroxide requires the presence of the water generated in the first step of the reaction (Equation 1) to form the amine nitrate.

$$(8)\ C_2H_5NCO + N_2O_4 \longrightarrow [C_2H_5N_2NO_3] + CO_2$$

$$(9)\ [C_2H_5N_2NO_3] \longrightarrow C_2H_5ONO_2 + N_2$$

$$(10)\ C_2H_5ONO_2 \longrightarrow C_2H_4 + HNO_3$$

EXPERIMENTAL

Reaction of ethanoyl hydrazide with dinitrogen tetroxide. Ethanoyl hydrazide,[5] m.p. 66.5–67.0°, 3.70 g. (0.05 mole), dissolved in 30 ml. of chloroform was placed in a 100 ml. 3-necked flask equipped with a dropping funnel, a gas inlet tube, and a gas exit tube leading to a gas buret. The system was flushed with dry nitrogen gas, cooled in an ice bath, and then 4.6 g. (0.05 mole) of dinitrogen tetroxide in 20 ml. of chloroform was added dropwise to moderate the vigorous reaction. A small sample of the reaction mixture was removed and found to give a strong positive test[6] for an azide. The ice bath was removed and the azide decomposed by warming gradually. The gases evolved were analyzed and found to contain 0.02 mole (40% theory) of carbon dioxide and 0.05 mole (100%) of additional nitrogen. The liquid product was distilled at 30° under diminished pressure (eventually 1 mm.). An aliquot of the distillate was titrated with base using phenolphthalein as an indicator. The results corresponded to 0.005 mole of monobasic acid, shown to be acetic acid by conversion to its phenylhydrazine derivative, m.p. 127–128° (lit. m.p. 128°).

The residue from the distillation solidified in part on cooling. Some of the solid was purified by recrystallization from ethanol and drying over phosphorus pentoxide under vacuum. It was identified as methylamine nitrate by its m.p. (108.0–108.5° in a sealed capillary tube), its mixture m.p. with an authentic sample, and its conversion to *N*-methyl-*N'*-phenylthiourea, m.p. 113°, by treatment with base and then with phenyl isothiocyanate. The nitrate radical was identified by conversion to sodium nitrate, m.p. 298–299°, on mixing with aqueous sodium hydroxide and evaporating to dryness. An aliquot of the distillation residue was submitted to a Van Slyke analysis[7] for a primary amine and yielded nitrogen gas corresponding to 0.028 mole (56% yield) of methylamine.

Reaction of butanoyl hydrazide with dinitrogen tetroxide. In an experiment similar to the above butanoyl hydrazide,[8] m.p. 46–47°, 24.5 g. (0.24 mole), in chloroform, 80 ml., was treated with dinitrogen tetroxide, 24.6 g. (0.275 mole), in chloroform, 60 ml., added over a period of 1.25 hr. At this time the solution gave a strong positive test for azide with ferric chloride solution. After warming carefully to decompose the azide, the product was distilled to remove the solvent and to obtain a small amount of butyric acid, 3.0 ml. The residue was extracted with ether, converted to propylamine with aqueous alkali, and to *N*-propyl-*N'*-phenylthiourea, m.p. 62° (yield 54% based on butanoyl hydrazide), with phenyl isothiocyanate. The aqueous alkali layer gave sodium nitrate, m.p. 298–299°, on evaporation and recrystallization.

Reaction of phenyl isocyanate with dinitrogen tetroxide. Phenyl isocyanate, 5.95 g. (0.05 mole), in chloroform, 120 ml., was treated with 4.6 g. (0.05 mole) of dinitrogen tetroxide in chloroform, 30 ml., at 0–5°. The unstable brownish crystals of benzenediazonium nitrate which formed were quickly filtered and dried on filter paper; yield, 4.7 g. (56% theory); m.p. 85° (detonation). They coupled with β-naphthol in basic solution to form the orange dye, 1-phenylazo-2-naphthol, m.p. 129–130°, and with β-naphthylamine to form 1-phenylazo-2-naphthylamine, m.p. 100°.

In another experiment using the same amounts of reactants the diazonium nitrate was not isolated and the reaction mixture was allowed to stand over night at room temperature. The gases evolved were collected in a gas buret and analyzed. They contained 0.038 mole (76%) of carbon dioxide. Evaporation of the solvent left a tar from which *o*-nitrophenol, 1.25 g. (18%), was isolated by extraction with base, acidification, and recrystallization from ligroin. It was identified by its m.p. of 45° and by conversion to 2-nitro-4-bromophenol, m.p. 116°.

Reaction of ethyl isocyanate with dinitrogen tetroxide. Ethyl isocyanate,[9] 25.27 g. (0.356 mole), was treated with 32.80 g. (0.356 mole) of dry dinitrogen tetroxide in 330 ml. of chloroform at 0–5°. The mixture was allowed to warm to room temperature and the evolved gases were collected in a gas buret. Analysis showed that they contained 0.290 mole (81.5%) of carbon dioxide, 0.314 mole (88.0%) of evolved nitrogen, and 0.018 mole (5.1%, based on one mole per mole of isocyanate) of ethylene. Distillation of the liquid product

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gave 13.0 g. of ethyl nitrate (40% theory), b.p. 85.0–85.4°, n_D^{23} 1.3834. Its infrared spectrum was identical with that for an authentic sample of ethyl nitrate.

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Reactions of Nucleophilic Reagents with Cyanuric Fluoride and Cyanuric Chloride

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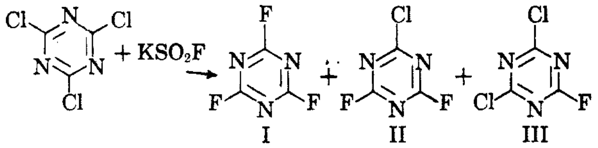
Recently, the preparation of cyanuric fluoride (I) was reported.[1] This novel compound was synthesized by reaction of cyanuric chloride with antimony trifluoride dichloride. It has been found in this laboratory that the action of potassium fluorosulfinate on cyanuric chloride yields a mixture of products as shown:



The physical properties observed are in essential agreement with those reported. Due to the novelty of the fluorine containing *s*-triazines, their infrared spectra are included, (Fig. 1).

Cyanuric chloride has long been known to react readily with nucleophilic reagents.[2] Cyanuric fluoride was reported to be hydrolytically unstable,[1] but its reactivity toward other reagents has not been established. Therefore, it was of interest to compare cyanuric fluoride and cyanuric chloride directly with respect to the replaceability of their halogens by certain bases. The results are summarized in Table I.

It can be seen that in contrast to the fluoride, the chloride yielded, in each case, a mixture of reaction products. The compositions of these mixtures were determined qualitatively by their amount of residual chloride coupled with previous evidence that nucleophiles (1–3) and (5) involve stepwise replacement of chlorine.[2] The reaction (4) of cyanuric chloride with water, differs in that the intermediate chlorohydroxy *s*-triazines are more easily hydrolyzed than cyanuric chloride.[3]

From the data given in Table I, it is concluded that with the general types of reagents illustrated by the examples used that cyanuric fluoride is qualitatively more reactive or as reactive as cyanuric chloride.

EXPERIMENTAL

Materials. Ether was of anhydrous analytical grade (Mallinckrodt). Tetrahydrofuran was purified by washing repeatedly with 40% sodium hydroxide solution, dried over calcium chloride, and then distilled from sodium. Gaseous ammonia (Matheson) was passed over sodium hydroxide pellets and used directly. Diethylamine was purified by distilling from sodium hydroxide pellets b.p. 55–56°, (lit. b.p. 55.5°).[4] Aniline was distilled from zinc dust. Methanol (Mallinckrodt Reagent Grade) was purified by the method of Vogel.[5] Cyanuric chloride (Matheson) was purified by preparing a saturated solution in dry chloroform, filtering off the insoluble solid and evaporating the filtrate to yield the pure material, m.p. 145–146°.

Apparatus. For the reactions of cyanuric fluoride and cyanuric chloride with the nucleophilic reagents, a Mini-Lab (Ace Glass Inc.) reaction assembly was used. To insure dryness, immediately before use, the apparatus was fitted with a drierite tube, flamed, and allowed to cool. All

TABLE I

REPLACEMENT OF THE HALOGENS OF CYANURIC FLUORIDE AND CYANURIC CHLORIDE BY NUCLEOPHILES UNDER IDENTICAL CONDITIONS

	Nucleophile	No. of Equivs.	Product from Cyanuric Fluoride	Yield %	Product from Cyanuric Chloride	Yield %
1	Ammonia[a]	. . .	2,4-Diamino-6-fluoro-*s*-triazine	90	2,4-Diamino-6-chloro-*s*-triazine and 2-amino-4,6-dichloro-*s*-triazine	. . .
2	Diethylamine	7.0	2,4-Bis(diethylamino)-6-fluoro-*s*-triazine	74	2,4-Bis(diethylamino)-6-chloro-*s*-triazine	100[b]
3	Aniline	6.0	Triphenylmelamine	100[b]	2,4-Bis(phenylamino)-6-chloro *s*-triazine	100[b]
4	Water	5.5	Cyanuric acid	94	Mixture of cyanuric acid and cyanuric chloride	. . .
5	Methanol[c]	3.0	2,4,6-Tris(methoxy)-*s*-triazine	77	2,4,6-Tris(methoxy)-*s*-triazine and 2-chloro-4,6-bis(methoxy)-*s*-triazine	. . .

[a] An indeterminate excess was used. [b] Crude product. [c] Potassium carbonate added as HCl acceptor.

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