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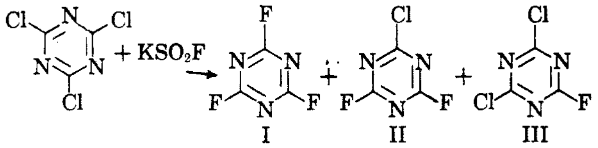
Recently, the preparation of cyanuric fluoride (I) was reported.[1] This novel compound was synthesized by reaction of cyanuric chloride with antimony trifluoride dichloride. It has been found in this laboratory that the action of potassium fluorosulfinate on cyanuric chloride yields a mixture of products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

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.

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

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(1) A. F. Maxwell, J. S. Fry, and L. A. Bigelow, *J. Am. Chem. Soc.*, **80**, 548 (1958).

(2) (a) J. T. Thruston, J. R. Dudley, I. Hechenbleikner, F. Schaefer, D. Holm-Hansen, *J. Am. Chem. Soc.*, **73**, 2981 (1951). (b) D. W. Kaiser, J. T. Thurston, J. R. Dudley, F. Schaefer, I. Hechenbleikner, and D. Holm-Hansen, *J. Am. Chem. Soc.*, **73**, 2984 (1951). (c) J. R. Dudley, J. T. Thurston, F. Schaefer, D. Holm-Hansen, C. Hull, and P. Adams, *J. Am. Chem. Soc.*, **73**, 2986 (1951) and other references contained therein.

(3) J. L. Comp, private communication.

(4) Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, N. Y., 1953, Vol. II, p. 180.

(5) A. Vogel, *Practical Organic Chemistry*, Longmans Green and Company, London, 1948, p. 168.

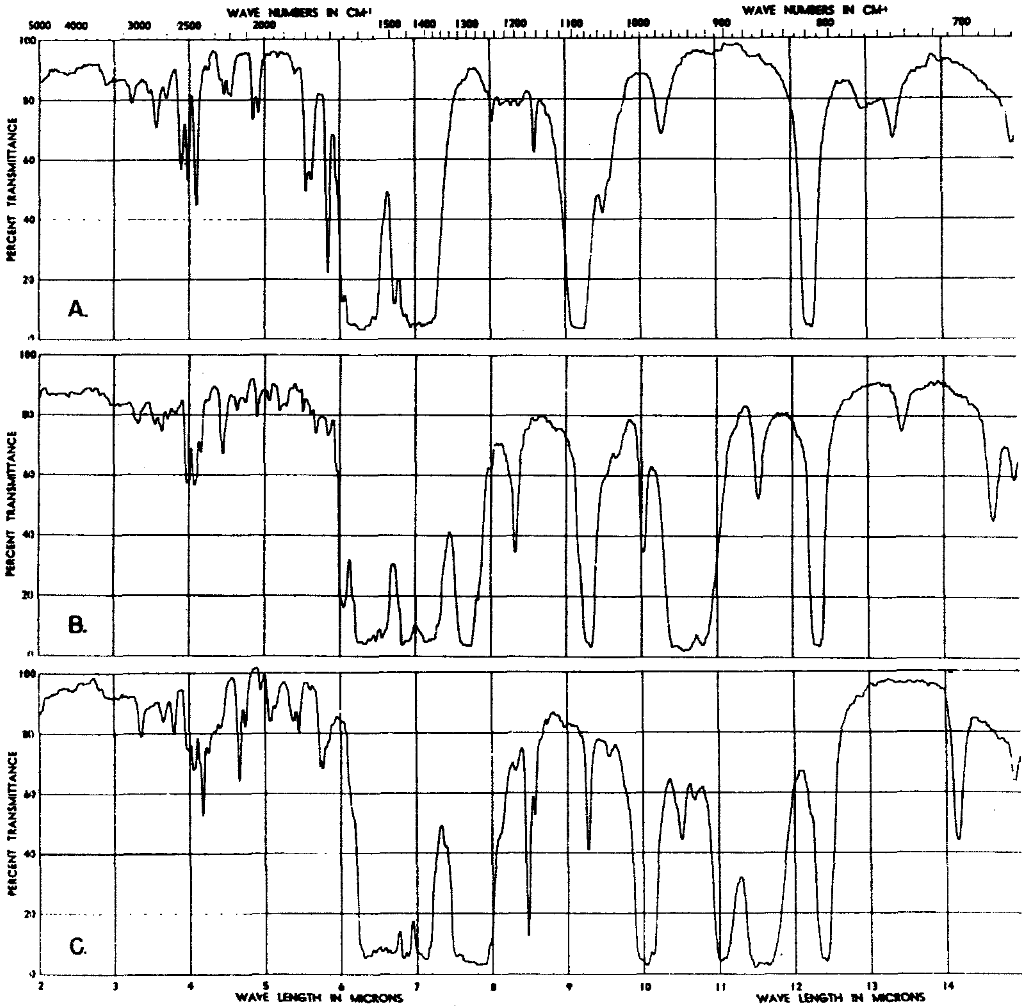

Fig. 1. Infrared absorption spectra (neat): Curve A, cyanuric fluoride; Curve B, 2-chloro-4,6-difluoro-*s*-triazine; Curve C, 2,4-dichloro-6-fluoro-*s*-triazine

operations were carried out in a well-ventilated hood because of the extreme odor and lacrymatory properties of the fluoro-*s*-triazines.

Cyanuric fluoride, 2-chloro-4,6-difluoro-s-triazine and 2,4-dichloro-6-fluoro-s-triazine. A finely-ground mixture of cyanuric chloride (368 g., 2 moles) and potassium fluorosulfinate (944 g.)[6,7] was placed in a flask equipped with a mechanical Hershberg stirrer and a distilling head connected to an ice-cooled receiver. The apparatus was protected from moisture by a drying tube. The stirred mixture was heated slowly with an oil bath to 120°. At this temperature, a colorless liquid began distilling from the reaction mixture. The temperature was maintained at 120° until the rate of distillation slowed noticeably; then the temperature was raised to 150° until distillation ceased. The clear distillate was redistilled through a 12″ helices-packed column. The following fractions were collected:

Cyanuric fluoride (85 g., 0.62 mole, 31% yield), b.p. 69–71°. This fraction was redistilled to yield the colorless, sharp smelling lacrymatory liquid (76.2 g., 0.56 mole, 28% yield), b.p. 69.5–70.8°,[8] (lit. b.p. 74°).[1]

Anal. Calcd. for $C_3F_3N_3$: C, 26.68; F, 42.21; N, 31.11. Found: C, 26.85; F, 42.41; N, 31.22.[9]

2-Chloro-4,6-difluoro-*s*-triazine (34 g., 0.22 mole, 11% yield), b.p. 107.8–109.5°, (lit. b.p. 113.5°).[1]

Anal. Calcd. for $C_3ClF_2N_3$: C, 23.79; Cl, 23.40; F, 25.08; N, 27.73. Found: C, 23.84; Cl, 23.16; F, 25.33; N, 27.49.

2,4-Dichloro-6-fluoro-*s*-triazine (6.2 g., 0.06 mole, 3% yield), b.p. 59–60°/20 mm., (lit. b.p. 155°).[1]

Anal. Calcd. for $C_3Cl_2FN_3$: C, 21.45; Cl, 42.22; F, 11.31; N, 25.01. Found: C, 21.62; Cl, 42.21; F, 11.12; N, 25.19.

Reactions of cyanuric fluoride and cyanuric chloride with nucleophilic reagents. Ammonia and cyanuric fluoride. Ammonia was passed into a solution of cyanuric fluoride (2.72 g., 20 mmoles) in ether (50 ml.) at 0° for 1 hr. The ether was evaporated *in vacuo* at room temperature and the residue washed with ice water, filtered, and the solid washed with acetone and then with ether. The white solid was dried at 50° *in vacuo* (20 mm.) to yield 2,4-diamino-6-fluoro-*s*-triazine (2.35 g., 18 mmoles, 90% yield).

Anal. Calcd. for $C_3H_4FN_5$: C, 27.90; H, 3.12; F, 14.72; N, 54.25. Found: C, 27.98; H, 3.20; F, 14.90; N, 54.25.

Ammonia and cyanuric chloride. The procedure was that used for cyanuric fluoride except that (3.68 g., 20 mmoles) of cyanuric chloride was used. The product was washed with water until the aqueous filtrate was free of chloride ion. The product was pressed dry on a suction filter with a rubber dam for 3 hr. and then dried at room temperature at 0.5 mm. to constant weight. There was obtained a white solid, crude 2,4-dichloro-6-amino-*s*-triazine (2.45 g., 15 mmoles, 75% yield).[10]

Anal. Calcd. for $C_3H_4ClN_5$: C, 24.76; H, 2.77; Cl, 24.37;

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(6) Seel, *Anorg. Chem.*, **282**, 293 (1955).

(7) Seel, *Angew. Chem.*, **68**, 461 (1956).

(8) All boiling points are uncorrected.

(9) Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

N, 48.14. *Anal.* Calcd. for $C_3H_2Cl_2N_4$: C, 21.73; H, 1.22; Cl, 42.79; N, 33.96. Found: C, 24.08; H, 2.62; Cl, 36.58; N, 36.48.

Diethylamine and cyanuric fluoride. A solution of cyanuric fluoride (1.36 g., 10 mmoles) in tetrahydrofuran (5 ml.) was added to a stirred solution of diethylamine (5.1 g., 70 mmoles) in tetrahydrofuran (25 ml.) at 20° during 15 min. The reaction mixture was stirred for an additional 80 min. The tetrahydrofuran then was evaporated *in vacuo* (surrounding bath at 60°) to yield an oily residue. This was stirred for 15 min. with 50 ml. of water, extracted with ether, and the organic layer was dried ($MgSO_4$), filtered, and evaporated *in vacuo* to yield a colorless solid. There was obtained 2,4-bis(diethylamino)-6-fluoro-*s*-triazine (1.77 g., 7.4 mmoles, 74% yield), m.p. 37–44°. A small amount of the material was sublimed (60°/0.5 mm.) to yield crystals, soften 37°, m.p. 44–45.5°.[10]

Anal. Calcd. for $C_{11}H_{20}FN_5$: C, 54.75; H, 8.35; F, 7.87; N, 29.03. Found: C, 54.79; H, 8.58; F, 8.08; N, 29.24.

Diethylamine and cyanuric chloride. The procedure was like that used for cyanuric fluoride except that (1.84 g., 10 mmoles) of cyanuric chloride was used. The oily solid was dissolved in chloroform and the chloroform extracted with water until the aqueous phase remained neutral. The organic layer was dried (Na_2SO_4), filtered, and evaporated *in vacuo* to yield an oil which was taken to constant weight (25°/0.5 mm.). There was obtained crude 2,4-bis-(diethylamino)-6-chloro-*s*-triazine, (2.57 g., 10 mmoles, 100%).[2a]

Anal. Calcd. for $C_{11}H_{20}ClN_5$: C, 51.24; H, 7.82; Cl, 13.75; N, 27.17. Found: C, 50.67; H, 8.05; Cl, 12.72; N, 26.19.

Aniline and cyanuric fluoride. Cyanuric fluoride (1.36 g., 10 mmoles) in tetrahydrofuran (10 ml.) was added over 5 min. to a stirred solution of aniline (5.58 g., 60 mmoles) in tetrahydrofuran (25 ml.) at room temperature. The reaction mixture was stirred for 2 hr. The tetrahydrofuran was evaporated *in vacuo* to yield a white solid which was triturated thoroughly with 5% HCl. The solid was filtered, washed with water until the filtrate remained neutral, and then dried *in vacuo* (80°/20 mm.) to constant weight. There was obtained crude triphenylmelamine (3.53 g., 10 mmole, 100%), soften 215°, m.p. 222–227°, (lit. m.p. 229–231°).[2b] A small sample was sublimed (140°/0.5 mm.) to yield a white crystalline sublimate I, m.p. 222-227°,[11] and a small amount of non-sublimated amorphous tan solid II, m.p. 300°.

Anal. Calcd. for I, $C_{21}H_{18}N_6$: C, 71.17; H, 5.12; N, 23.71. Found: C, 69.74; H, 5.47; N, 19.98; F. 0.00.

Aniline and cyanuric chloride. The procedure and work-up followed those used for cyanuric fluoride except that (1.84 g., 10 mmoles) of cyanuric chloride was used. The white solid was dried at (25°/0.5 mm.) to constant weight. There was obtained crude 2,4-bis(phenylamino)-6-chloro-*s*-triazine (3.05 g., 10 mmoles, 100%), m.p. 187–191°, (lit. m.p. 199–201°).[2a]

Anal. Calcd. for $C_{15}H_{12}ClN_5$: C, 60.49; H, 4.06; Cl, 11.91, N, 23.52. Found: C, 61.99; H, 4.49; Cl, 9.16; N, 22.89.

Water and cyanuric fluoride. A solution of cyanuric fluoride (2.72 g., 20 mmoles) in tetrahydrofuran (10 ml.) was added to a stirred solution of water (2.0 g., 110 mmoles) in tetrahydrofuran (25 ml.) at 0° over 10 min. The tetrahydrofuran was evaporated at room temperature *in vacuo* to yield a white solid which was dried *in vacuo* (25°/0.5 mm.) to constant weight. There was obtained cyanuric acid (2.45 g., 18.8 mmoles, 94%).

Anal. Calcd. for $C_3H_3N_3O_3$: C, 27.91; H, 2.34; N, 32.55. Found: C, 27.74; H, 2.56; N, 32.47; F, 0.00.

Water and cyanuric chloride. The procedure and work-up were those used for cyanuric fluoride except that (3.69 g., 20 mmoles) of cyanuric chloride was used. There was obtained a white solid, a mixture of cyanuric chloride and cyanuric acid[12] (3.33 g.).

Anal. Calcd. for $C_3Cl_3N_3$: C, 19.54; Cl, 57.70; N, 22.79. Found: C, 20.76; H, 3.07; Cl, 48.07; N, 23.25.

Methanol and cyanuric fluoride. A solution of cyanuric fluoride (2.78 g., 20 mmoles) in tetrahydrofuran (10 ml.) was added to a stirred mixture of anhydrous potassium carbonate (8.2 g., 60 mmoles) and methanol (25 ml.) at 10° over 5 min. The reaction mixture was stirred for 2 hr. at room temperature, filtered, and the residue I was washed with chloroform. The chloroform was combined with the filtrate; the resulting mixture was evaporated *in vacuo* at room temperature to yield a white solid II. The solid II was triturated with cold water (50 ml.), pressed dry on a filter, and dried to constant weight *in vacuo* (95°/20 mm.). There was obtained 2,4,6-tris(methoxy)-*s*-triazine (2.65 g., 15.5 moles, 77%), m.p. 133–135.5°, (lit. m.p. 134–136°).[2c]

Anal. Calcd. for $C_6H_9N_3O_3$: C, 42.10; H, 5.29; N, 24.55. Found: C, 42.04; H, 5.44; N, 24.42.

Methanol and cyanuric chloride. The procedure and work-up were those used for cyanuric fluoride except (2.68 g., 20 mmoles) of cyanuric chloride was used. The white solid was dried to constant weight on a suction filter with a rubber dam. There was obtained crude 2,4,6-tris(methoxy)-*s*-triazine (2.03 g., 12 mmoles, 60%), m.p. 94–120° (lit. m.p. 134–136°).[2c]

Anal. Calcd. for $C_5H_6ClN_3O_2$: C, 34.20; H, 3.45; Cl, 20.20, N, 23.93. Found: C, 39.43; H, 4.84; Cl, 5.43; N, 21.45.

Acknowledgment. The authors gratefully acknowledge the assistance of the infrared spectroscopy group of Dr. William Cave and also wish to thank W. Morgan Padgett for several valuable suggestions concerning this work.

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[10] All melting points were taken with a Fisher-Johns melting point apparatus and are uncorrected.

[11] Repeated recrystallization from hot 1-butanol did not improve the purity of the product.

[12] The infrared spectrum of the solid (KBr disk) contained all the bands of cyanuric chloride in addition to those of cyanuric acid.

Synthesis of 2-Chlorophenothiazine *via* a Smiles Rearrangement[1]

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2-Chlorophenothiazine (I) is the parent compound of chloropromazine [2-chloro-10-(3-dimethylaminopropyl)phenothiazine] (II) and of related biologically active substances. The principal method of preparation of 2-chlorophenothiazine involves the reaction of 3-chlorodiphenylamine with sulfur.[3] Both the 2-chloro and 4-chloro isomers are obtained from this reaction; the 2-chloro derivative

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[1] Abstracted from an undergraduate research project of Robert J. Galbreath, Ohio University, 1957.

[2] Present address: School of Medicine and Dentistry, The University of Rochester.

[3] P. Charpentier, P. Gailliot, R. Jacob, J. Gaudechon, and P. Buisson, *Compt. rend.*, **235**, 59 (1952); P. Charpentier, U. S. Patent **2,645,640** [*Chem. Abstr.*, **49**, 3268 (1955)]; British Patent **716,205** [*Chem. Abstr.*, **50**, 1929 (1956)].