rates were run at least in duplicate and many in triplicate. The average deviations were less than 6% with one exception. The rapid rate of oxidation of **2** led to experimental difficulties and here the average deviation was 10%. In addition, relative rates were run on a preparative scale using a modification of the Brown and Garg oxidation procedure[11] comparing **1** and **3** with *exo*-2-norbornanol and **5** with **8**. In all cases, the relative rates were in good agreement with the results reported and the products checked by vapor phase chromatography (vpc) were present in high yield with no rearrangement.

Registry No.—**1,** 10271-42-8; **2,** 10271-43-9; **3,** 10271-44-0; **4,** 10271-45-1; **5,** 10271-46-2; **6,** 10271-47-3; **7,** 10271-48-4; **8,** 10271-49-5; *exo*-2-norbornanol, 497-37-0; *endo*-2-norbornanol, 497-36-9; cyclopentanol, 96-41-3.

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[11] H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

Fluorocarbon Nitrogen Compounds. XII. Catalytic Perfluoroalkylation of Halotriazines[1]

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Perfluoro olefins react with carbonyl fluoride in the presence of fluoride ion to give perfluoroacyl fluorides and perfluoro ketones.[2] Compounds containing fluorine atoms whose reactivity is comparable to that of an acid fluoride, in structures otherwise inert toward fluoride ion, should undergo analogous reactions. The halotriazines are in some respects similar to acid halides, and fluorotriazines readily undergo fluoride-catalyzed reaction with polyfluoro compounds containing carbon–carbon or carbon–nitrogen unsaturation.

Cyanuric fluoride, heated under autogenous pressure with perfluoropropene and cesium fluoride at 100° for 12 hr, was converted almost quantitatively (>90%) to a mixture of mono-, bis-, and tris(perfluoroisopropyl)-triazines, easily separable by fractionation. Although three compounds were formed, the reaction could be directed toward any one of the three by altering the reactant ratio. With a $C_3F_6:(CNF)_3$ ratio of approximately 2:1, the ratio of mono-, di-, and trisubstitution products was 8:10:1, while a reactant ratio of 1:1.25 led to a product ratio of 28:6:1.

All of the products showed the characteristic triazine absorption band near 1550 cm^{-1}. Both the complexity of this band and its intensity relative to absorption by the $(CF_3)_2CF$ groups decreased with increasing degree of substitution. In nuclear magnetic resonance (nmr) spectra, chemical shifts for the ring fluorine, the CF_3 of $(CF_3)_2CF$ and the CF of $(CF_3)_2CF$ were, respectively, 30.4–30.6, 74.4–75.4, and 183.8–186.5 ppm upfield from $CFCl_3$, as perfluoroisopropyl groups were added. Fine structure and area ratios for the three different types of fluorine were consistent with the assigned structures.

Functionally active perfluoroalkyl side chains can be introduced into a triazine ring in the same manner, as long as these functions are inert to fluoride ion. Perfluoroallyl cyanide, made by dehalogenation of $CF_2ClCFClCF_2CN$, reacted under the same conditions with a slight excess of 2,4-bis(perfluoroisopropyl)-6-fluoro-*s*-triazine to give a 62% yield of perfluoro-[2-(β-cyanoisopropyl)-4,6-diisopropyl]triazine.

Compounds containing unsaturation other than carbon–carbon can also be utilized. Perfluoro-2-azapropene ($CF_3N{=}CF_2$) reacted with cyanuric fluoride in a manner entirely analogous to that of perfluoropropene and produced a mixture of mono-, bis-, and tris(perfluorodimethylamino)-substituted triazines, a 2:1 $CF_3N{=}CF_2:(CNF)_3$ ratio giving a product ratio of 1:2:1. Infrared spectra showed the same sequential behavior of the 1550-cm^{-1} band as with the perfluoroisopropyl series; in the monosubstituted compound this band was a multiplet, in the disubstituted compound a doublet, and in the symmetrical trisubstituted compound a singlet. Nmr spectra showed peaks for the $(CF_3)_2N$ and ring fluorine atoms at 55.1, 55.0, and 32.4, 32.9 ppm, relative to $CFCl_3$, for the mono- and disubstituted compounds, while the trisubstituted compound showed only a 55.2-ppm peak. Area ratios for (side chain:ring) fluorine were in the correct ranges, 6:2 and 12:1, respectively. As was the case with the perfluoroisopropyl series, the trisubstituted compound was a low-melting solid.

Physical constants of the substituted triazines are given in Table I.

A fluorine atom on an aromatic or heterocyclic ring must apparently be fairly labile for the alkylation to succeed. Neither perfluorobenzene nor bromopentafluorobenzene reacted with either $CF_3CF{=}CF_2$ or $CF_3N{=}CF_2$ when heated in the presence of cesium fluoride, either alone or in acetonitrile solution, at temperatures up to 175°. It is possible that the *p*-fluorine atom in nitropentafluorobenzene might be reactive enough to permit alkylation, although this compound was not investigated. Cyanuric chloride could probably be substituted for cyanuric fluoride, since the former is converted to the latter by alkali metal fluorides, although this technique would obviously require the use of sufficient fluoride for both halogen exchange and catalysis.

The carbanion reaction mechanism advanced by Smith[2] to explain the carbonyl fluoride–olefin reactions seems consistent with the present results as well. Attack of fluoride ion on the terminal carbon atom of the unsaturated group would lead to a branch at the α carbon (or nitrogen) of the substituent group in the substituted triazine, as has been observed in every case.

Experimental Section

Perfluoroalkylation of Cyanuric Fluoride.—Cesium fluoride (50 g) was dried in an autoclave at 200–300° overnight under continuous evacuation. The bomb was cooled and loaded by vacuum transfer with 45 g (0.33 mole) of cyanuric fluoride and 87.5 g (0.58 mole) of hexafluoropropene, then sealed and rocked at 100° for 16 hr.

The cooled bomb was vented into an evacuated system, giving <1 g of volatile material. The crude product was decanted and the residual solid extracted with Freon 113, 126 g (95%) of the

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[1] Presented in part at the 150th National Meeting of the American Chemical Society, New York, N. Y., Sept 12–16, 1966. Previous paper: J. A. Young and R. L. Dressler, *J. Org. Chem.*, in press.

[2] R. D. Smith, F. S. Fawcett, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4285 (1962).

TABLE I
PHYSICAL CONSTANTS OF SUBSTITUTED TRIAZINES

Position 2	4	6	Bp, °C (mm)	n^{25}_D	Registry no.
i-C_3F_7	F	F	99–100 (630)	1.3131	10271-35-9
i-C_3F_7	i-C_3F_7	F	125–126 (630)	1.3373	10271-36-0
i-C_3F_7	i-C_3F_7	i-C_3F_7	137–138[a] (630)	. . .	10271-37-1
$(CF_3)_2N$	F	F	108–109 (630)	1.3477	10271-38-2
$(CF_3)_2N$	$(CF_3)_2N$	F	73–75 (40)	1.3485	10271-39-3
$(CF_3)_2N$	$(CF_3)_2N$	$(CF_3)_2N$	90[b] (40)	. . .	10271-40-6
$CF(CF_3)CF_2CN$	i-C_3F_7	i-C_3F_7	79–80 (20)	1.3266	10271-41-7

[a] Mp 30–31. [b] Mp 47–48.

initial 132.5 g being recovered. The material was fractionated through a 1-ft column of metal helices to give the monoalkylated product in 39% conversion, the dialkylated product in 51% conversion, and the trialkylated product in 5% conversion.

Although the structures of all three compounds were established unequivocally by nmr and infrared spectra, elemental analyses on the mono- and dialkylated products were unsatisfactory except for nitrogen values, possibly because of hydrolysis of the very moisture-sensitive ring fluorine atoms since the trialkylated product gave satisfactory results.

Anal. Calcd for $C_{12}F_{21}N_3$: C, 24.6; F, 68.2; N, 7.2. Found: C, 24.6; F, 68.0; N, 7.3.

Cyanoperfluoroalkylation of 2,4-Bis(perfluoroisopropyl)-6-fluoro-*s*-triazine.—A pressure vessel containing 10 g of dried cesium fluoride was loaded by siphoning in under partial vacuum 14 g (0.032 mole) of the above triazine and adding by vacuum transfer 4.5 g (0.028 mole) of perfluoroallyl cyanide. It was then sealed and rocked for 24 hr at 100°. The crude product was decanted, combined with Freon 113 extracts of the residual solid, and fractionated to give 10.4 g (61.5%) of the addition product.

Anal. Calcd for $C_{13}F_{20}N_4$: C, 26.4; N, 9.5. Found: C, 26.7; N, 9.8.

Perfluorodimethylamination of Cyanuric fluoride.—A pressure vessel containing 50 g of dried cesium fluoride was loaded, as described above, with 10 g (0.075 mole) of cyanuric fluoride and 20 g (0.15 mole) of perfluoro-2-azapropene. After agitation at 110° for 26 hr it was evacuated through a cold trap for 6 hr. The residual material was extracted with two 25-ml portions of Freon 113, the solvent was removed, and the liquid residue was combined with that obtained during the evacuation. Fractionation through a vacuum-jacketed Vigreux column gave, in addition to intercuts, 3.8 g (19% conversion) of the monosubstituted compound, 8.5 g (29% conversion) of the disubstituted compound, and 4.3 g (16% conversion) of the trisubstituted compound, all at least 88% pure. Since no extraneous peaks appeared in chromatograms of any of the intercuts, and material balance was good, the apparent conversion figures would be raised appreciably by more efficient separation.

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Triglycidyl Isocyanurate Synthesis Using Dispersed Caustic

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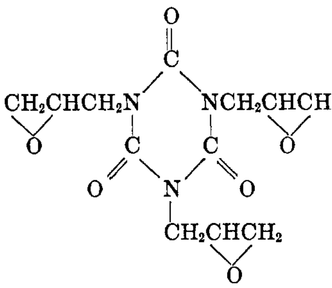
The products from the reaction of cyanuric acid with epichlorohydrin have been dehydrohalogenated by a variety of methods to give epoxy compositions.[1] Recent publications[2] indicate that crystalline triglycidyl isocyanurate, or tris(2,3-epoxypropyl)-*s*-triazine-2,4,6-(1H,3H,5H)-trione, may be obtained as a mixture of two racemic modifications by this general preparative route. The procedure below also permits the isolation of crystalline triglycidyl isocyanurate (I) and illustrates the use of a novel dispersed form of sodium hydroxide for dehydrohalogenation.



I

A stable dispersion of caustic in an aprotic medium may be prepared if a small amount of a fatty acid is employed as a dispersing aid. Particle diameters under 15 μ have been obtained in benzene, mineral spirits, dioxane, and xylene. Such dispersions can be metered into a reactor with a chemical proportioning pump, and permit a more rapid reaction or use of a lower reaction temperature than other solid forms of caustic in the preparation of triglycidyl isocyanurate. Other reactions involving additions of solid caustic can perhaps be similarly facilitated by use of the dispersed form of the reagent.

Experimental Section

Caustic Dispersion.—A mixture of 400 g of 96% flake sodium hydroxide, 4 g of dimerized fatty acid, and 600 g of xylene was ground overnight in a pebble mill[3] with a 60-rpm speed. The dispersion was stored in a glass container after removal of the pebbles. Standardization and metering by volume proved feasible if the stored dispersion was shaken by hand before sampling and xylene was used as a wash liquid to complete a transfer.

Crystalline Triglycidyl Isocyanurate (I).—A mixture of 129 g (1.0 mole) of cyanuric acid, 1388 g (15.0 mole) of epichlorohydrin, and 7 ml of a 60% aqueous solution of benzyltrimethylammonium chloride was heated until a self-sustaining exothermic reaction was established at 113°. When the reaction temperature began to drop after about 10 min, heat was again applied to maintain reflux conditions for 1 hr. The above caustic dispersion (3 equiv, 308 ml) was then added over 1.5 hr to the stirred mixture at ambient temperature between 31 and 51°. Water was then azeotropically distilled from the reactor at overhead temperatures up to 120°, and the cooled residue was filtered to remove salt. The excess epichlorohydrin was subsequently distilled off at pot temperatures up to 122° at 35 mm and replaced by 400 ml of methyl ethyl ketone.

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(1) U. S. Patent 2,809,942; U. S. Patent 2,931,781; French Patent 1,394,438; British Patent 996,724.

(2) M. Budnowski, *Kunststoffe*, **55**, 641 (1965); German Patent 1,211,650.

(3) Neck-type ABCO porcelain jar of the Abbe Engineering Co., with size B-2 flint pebbles and 1-qt rated capacity.