Fluorocarbon Nitrogen Compounds. XI. Functionally Active Perfluoroalkyl-Substituted *s*-Triazines[1]

John A. Young and Robert L. Dressler

Chemical Division, Denver Research Institute, University of Denver, Denver, Colorado

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s-Triazines containing one or two perfluoroallyl groups were prepared by a seven-step synthesis starting from $CF_2ClCFClCF_2CFCl_2$. The perfluoroalkenyltriazines added mercuric fluoride and the resulting mercurials were converted to iodoperfluoroalkyltriazines. Polymeric materials were obtained from difunctional alkenyltriazines by addition of mercuric fluoride or perfluoroglutaryl fluoride, from bis(iodoperfluoroalkyl)triazines by photochemical coupling, and from bis(cyanoperfluoroalkyl)triazines by reaction with silver difluoride. Perfluoroalkyl-substituted fluorotriazines reacted with cyanide ion to form cyanotriazines; silver difluoride reversed this exchange. When the cyano group was separated from the triazine ring by a perfluoroalkylene segment, normal fluorination to an azo group apparently occurred.

Perfluoroalkyl-*s*-triazines can be prepared by thermal trimerization of perfluoronitriles[2] or perfluoroimidoylamidines,[3] or by ring closure of the latter with acid chlorides[4] or acid anhydrides;[5] however, no perfluoro compounds containing functional groups in the side chains have been reported. This paper describes the synthesis of mono- and difunctional perfluoroalkenyltriazines and some of their reactions.

Perfluoroalkenyltriazines were made by synthesizing *s*-triazines with two (*vic*-dichloro)perfluoroalkyl substituents and subsequently dehalogenating these compounds. The most convenient starting point was 3,4-dichloroperfluorobutyric acid, but since this acid was not commercially available it was made by hydrolysis of $CF_2ClCFClCF_2CFCl_2$ in oleum[6] and converted without isolation to the ethyl ester. The ester was then subjected to ammonolysis and the resulting amide dehydrated to the nitrile, both reactions by conventional means. The over-all yields for the hydrolysis and esterification reactions averaged about 50% while the last two steps were virtually quantitative. Low-temperature reaction of the nitrile with 0.5 mole of ammonia gave an imidoylamidine which was converted without isolation to a triazine by ring closure with trifluoroacetic or perfluorobutyric anhydride, yielding a perfluoro[2,4-bis(2,3-dichloropropyl)-6-methyl (or -6-propyl)]-*s*-triazine. Over-all conversions of nitrile to triazine averaged 75–80% although yields as high as 93% were sometimes obtained.

The perfluorobis(dichloropropyl)triazines were dehalogenated by use of zinc in dioxane. Acceptable yields (70–75%) were usually obtained but occasionally the intermediate perfluoro(2-allyl-4-dichloropropyl) compound was the main product, and no method of activating the zinc was found which gave entirely consistent results. The intermediate compound could be further dehalogenated to the perfluorodiallyltriazine in about the same yield by repeating the treatment with zinc. Vapor phase dehalogenation over hot iron was also investigated; the results summarized in Table I indicate that a satisfactory procedure might be developed with an optimum temperature in the neighborhood of 450°, but dehalogenation in solution was the preferred method.

Table I

Vapor Phase Dehalogenation of Perfluoro[2,4-bis(dichloropropyl)-6-methyl]-*s*-triazine

Reaction temp, °C	Triazine content of product, %			
	2,4-$(CF_2{=}CFCF_2)_2$	2-$CF_2{=}CFCF_2$, 4-$CF_2ClCFClCF_2$	2,4-$(CF_2ClCFClCF_2)_2$	Other components
300	0	0	100	0
400	0.7	14	81	4
500	16	29	24	28

The perfluoroallyltriazines underwent oxidation at the carbon–carbon double bond very readily, but isolation of triazine carboxylic acids was unsuccessful with nitric acid, potassium permanganate, or chromic acid as oxidant, presumably because of hydrolytic decomposition of the triazine ring during product work-up. Oxidation by chlorine and oxygen with simultaneous ultraviolet irradiation gave good yields of triazinecarboxylic acid fluorides but it proved impossible to oxidize both double bonds in a single molecule; chlorinolysis or addition of chlorine occurred and no difunctional chlorine-free acid fluorides were isolated.

Preparations of bis(iodoperfluoroalkyl)triazines from perfluoroallyltriazines by S_N2' reaction with iodide ion,[7] by addition of iodine monofluoride,[8] or by fluoride-catalyzed reaction with iodine[9] were uniformly unsuccessful. With the first two reagents no reaction took place, while cesium fluoride or potassium fluoride when warmed with a perfluoroallyltriazine caused immediate color formation and eventual appearance of a black solid. No reaction occurred with cesium fluoride when a saturated perfluoroalkyltriazine was substituted for the perfluoroallyl compound. Epoxidation and homopolymerization by peroxide or γ-ray initiation were also unsuccessful.

Ultraviolet irradiation of a mixture of perfluoro(2,4-diallyl-6-propyl)-*s*-triazine with perfluoroglutaryl fluoride led to the formation of solid films and high-boiling liquids, about one-half the triazine charged

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[1] Presented at the 150th National Meeting of the American Chemical Society, New York, N. Y., Sept 1966. For the previous paper in this series, see J. A. Young and R. D. Dresdner, *J. Org. Chem.*, **28**, 833 (1963).

[2] W. L. Reilly and H. C. Brown, *ibid.*, **22**, 698 (1957).

[3] H. C. Brown, U. S. Patent 3,086,946; *Chem. Abstr.*, **59**, 9813 (1963). See also *U. S. Govt. Res. Rept.*, **36**, (3), 12 (1961).

[4] H. C. Brown, 147th Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

[5] E. Dorfman, W. E. Emerson, R. L. K. Carr, and C. T. Bean, Spring Meeting Rubber Division of the American Chemical Society, San Francisco, Calif., May 1966.

[6] The authors are indebted to Dr. R. J. Seffl of the 3M Co. for details of this procedure.

[7] A. H. Fainberg and W. T. Miller, Jr., *J. Am. Chem. Soc.*, **79**, 4164 (1957).

[8] M. Hauptschein and M. Braid, *ibid.*, **83**, 2383 (1961); R. D. Chambers, W. K. R. Musgrave, and J. Savory, *J. Chem. Soc.*, 3779 (1961).

[9] C. G. Krespan, *J. Org. Chem.*, **27**, 1813 (1962).

TABLE II

PHYSICAL CONSTANTS OF SUBSTITUTED TRIAZINES

Compd	Registry No.	Position			Bp, °C	Pressure	$n^{25}{}_{D}$
		2	4	6			
1	10407-78-0	CF_3	CN	CN	57–59[a]	0.3 mm	
2	10407-79-1	i-C_3F_7	i-C_3F_7	CN	66–67	10 mm	
3	10407-80-4	i-C_3F_7	CN	CN	Mp 87–88		
4	10407-81-5	CF_3	$CF_2ClCFClCF_2$	$CF_2ClCFClCF_2$	65	50 μ	1.3890
5	10407-82-6	C_3F_7	$CF_2ClCFClCF_2$	$CF_2ClCFClCF_2$	92	3 mm	1.3760
6	10407-83-7	CF_3	$CF_2{=}CFCF_2$	$CF_2ClCFClCF_2$	80[b]	10 mm	1.3585[b]
7	10407-84-8	C_3F_7	$CF_2{=}CFCF_2$	$CF_2ClCFClCF_2$	73	3 mm	1.3603
8	10407-85-9	CF_3	$CF_2{=}CFCF_2$	$CF_2{=}CFCF_2$	60	10 mm	1.3553
9	10421-82-6	C_3F_7	$CF_2{=}CFCF_2$	$CF_2{=}CFCF_2$	52	3 mm	1.3450
10	10407-86-0	C_3F_7	CF_3CFICF_2	$CF_2ClCFClCF_2$	60	50 μ	
11	10407-87-1	CF_3	CF_3CFICF_2	CF_3CFICF_2	55	40 μ	1.4163
12	10407-88-2	C_3F_7	CF_3CFICF_2	CF_3CFICF_2	53	50 μ	1.3866
13	10407-89-3	CF_3	$(CF_2)_6CN$	$(CF_2)_6CN$	105	1 mm	
14	10535-62-3	C_3F_7	$CF(CF_3)CF_2$[c]	$CF_2ClCFClCF_2$	145	100 μ	1.3710
15	10407-90:6	C_3F_7	$HgCF(CF_3)CF_2$[d]	$CF_2ClCFClCF_2$	150	50 μ	

[a] Mp 70–71. [b] Product impure, unreliable value. [c] Coupled product from **10**. [d] Mercurial from **7**.

reacting over a period of 9 days. Infrared spectra of the products showed absorptions due to triazine ring, C=C unsaturation, and COF groups. Since neither of the reactants behaved in this manner when irradiated alone and the usual mode of photochemical reaction between an unsaturated fluorocarbon and a carbonyl compound is oxetane formation, these materials may have been polyoxetanes.

Like other fluorocarbon olefins, the perfluoroallyltriazines readily added mercuric fluoride. Perfluoro-(2-allyl-4-dichloropropyl-6-propyl)-*s*-triazine gave a stable, low-melting adduct which in spite of its high molecular weight (1400) could be distilled without decomposition, while perfluoro(2,4-diallyl-6-propyl)-*s*-triazine gave a polymeric mercurial which was a colorless brittle solid at room temperature, slightly soluble in Freon 113 and benzene, very soluble in polar organic solvents and anhydrous hydrogen fluoride, and attacked slowly by boiling 1:1 hydrochloric acid. Treatment with iodine at 120° converted the monomeric and polymeric mercurials to mono- and bis(iodoperfluoroalkyl)triazines, respectively. The latter were more conveniently made without isolation of the intermediate mercurial, merely by removing the hydrogen fluoride (HF) used as solvent in the reaction with mercuric fluoride and treating the crude polymer with iodine.

The iodoperfluoroalkyltriazines so obtained underwent coupling when irradiated in the presence of mercury. From perfluoro[2-(2-iodopropyl)-4-(2,3-dichloropropyl)-6-propyl]-*s*-triazine the coupled product, a viscous liquid, bp 135° (100 μ), was produced in 83% yield. Similar coupling of a bis(iodoperfluoroalkyl)-triazine gave a glass rather than an elastomer, probably because of impurities in the monomer since the latter on chromatographic analysis proved to be only 80% one component. The bis(iodoperfluoroalkyl) compounds could also be polymerized slowly by irradiation at reflux *in vacuo*, iodine being pumped off as formed. A rather resilient solid obtained in this manner showed no visually detectable change below 270°. Since this sample did not melt below 400°, some cross linking may have occurred during polymerization; however, infrared absorption at 1550 cm^{-1} indicated that the triazine ring was still present.

2,4-Difluoro-6-trifluoromethyl-*s*-triazine was made by the method of Grundmann,[10] although considerable coupling of the intermediate dichloromethyltriazine through CCl_2 groups was encountered in chlorination of 2,4-dichloro-6-methyl-*s*-triazine. A much more efficient route to perfluoroalkyl-substituted halotriazines was found in the fluoride-catalyzed perfluoroalkylation of halotriazines with hexafluoropropene,[11] by which perfluoroisopropyldifluoro- and bis(perfluoroisopropyl)-fluorotriazines could be prepared in good yields from cyanuric fluoride. Attempts to alkylate cyanuric fluoride by using trifluorovinyllithium or trifluorovinylmagnesium bromide failed, producing only tars.

The perfluoroalkylfluorotriazines were easily converted to perfluoroalkylcyanotriazines by treatment with sodium cyanide in acetonitrile. Reaction of the cyanotriazines with silver difluoride, however, resulted merely in replacement of CN by F, indicating that a cyano group must be separated from a triazine ring by a perfluoroalkylene segment in order to undergo the fluorination to an azo linkage which is characteristic of fluorocarbon nitriles. Triazines of this last type were made in two ways. In an extension of the catalyzed perfluoroalkylation reaction, 2-fluoro-4,6-bis(perfluoroisopropyl)-*s*-triazine was treated with perfluoroallyl cyanide to give perfluoro-[2-(β-cyanoisopropyl)-4,6-diisopropyl]-*s*-triazine in 62% yield,[11] while a bis(cyanoperfluoroalkyl)triazine was made by reacting perfluorosuberonitrile with 0.5 mole of ammonia and then cyclizing the resulting imidoylamidine with trifluoroacetic anhydride to give perfluoro-[2,4-bis(6-cyanohexyl)-6-methyl]-*s*-triazine.[12] Reaction of these two cyanoperfluoroalkyltriazines with silver difluoride indicated successful fluorination of C≡N to $CF_2N{=}NCF_2$, although the products were obtained in amounts inadequate for purification and complete characterization. In each case spectral absorption attributable to an azo linkage (1750 cm^{-1}, 381 mμ[13]) made its appearance and the products were yellow, as perfluoro azo compounds usually are. In addition, a nuclear magnetic resonance (nmr) spectrum of the product from perfluoro-[2-(β-cyanoisopropyl-4,6-diisopropyl]-*s*-triazine showed a new peak in the CF_2 region, at a δ value consistent with a $CF_2N{=}NCF_2$ structure (63.7 ppm relative to $CFCl_3$), and indicated that a dimeric molecule had been formed. This product, after distil-

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(10) C. Grundmann and E. Kober, *J. Am. Chem. Soc.*, **79**, 944 (1957).

(11) R. L. Dressler and J. A. Young, *J. Org. Chem.*, **32**, 0000 (1967).

(12) This reaction was first ca ried out by the Hooker Chemical Corp. The authors are grateful to Dr. Russell L. K. Carr for the sample of perfluorosuberonitrile.

(13) P. Robson, V. C. R. McLoughlin, J. B. Hynes, and L. A. Bigelow, *J. Am. Chem. Soc.*, **83**, 5010 (1961).

TABLE III

NMR CHEMICAL SHIFTS (δ) IN SUBSTITUTED TRIAZINES[a]

Compd	Registry No.	No.	Substituents of 1,3,5-triazine in position 2	4	6	$\mathit{CF_3}$–$\mathrm{CF_2}$	$\mathit{CF_3}$–$\mathrm{CFCF_3}$	$\mathit{CF_3}$–CFI	$\mathit{CF_3}$–T	$\mathit{CF_2}$–$\mathrm{CF_3}$	$\mathit{CF_2}$–TCFCl	$\mathit{CF_2}$–T	$\mathit{CF_2}$–CF	$\mathit{CF_2}$–Cl	CF–$\mathrm{CF_3CF_3}$	CF–T	CF–$\mathrm{CF_2}$	CF–Cl	F–T
1	675-14-9	1	F	F	F														20.8
2	696-85-5	2	Cl	F	F														33.5
3		3	CF_3	CN	CN				73.2										
4	10271-35-9	4	i-C_3F_7	F	F		74.4								183.8				30.4
5		5	i-C_3F_7	CN	CN		74.5								186				
6	10271-36-0	6	i-C_3F_7	i-C_3F_7	F		75.6								187				30.6
7		7	i-C_3F_7	i-C_3F_7	CN		74.8								187				
8	10271-37-1	8	i-C_3F_7	i-C_3F_7	i-C_3F_7		75.4								186.5				
9	10407-95-1	9	i-C_3F_7	i-C_3F_7	$CF_2CF(CF_3)CN$		73.4	79.0[b]			118.8[c]				182.1, 167.8[d]				
10		10	CF_3	$CF_2ClCFClCF_2$	$CF_2ClCFClCF_2$				73.2		111			63.7				132	
11		11	CF_3	$CF_2{=}CFCF_2$	$CF_2{=}CFCF_2$				71.5			105	97.5				167		
12		12	CF_3	CF_3CFICF_2	CF_3CFICF_2			72.6	71.6			103				143			
13		13	n-C_3F_7	$CF_2ClCFClCF_2$	$CF_2ClCFClCF_2$	79				124.5	115	107		61.8				128	
14		14	n-C_3F_7	$CF_2{\cdot}CFCF_2$	$CF_2{\cdot}CFCF_2$	83.5				129.1	119.7	103.5	99.3						
15		15	n-C_3F_7	CF_3CFICF_2	CF_3CFICF_2	80.6		72.9		125.9		103.8				144.3			

[a] CCl_3F as internal standard ($\delta = 0$). T = triazine ring. [b] $\mathit{CF_3}$ in $CF_2CF(CF_3)CN$. [c] $\mathit{CF_2}$ in $CF_2CF(CF_3)CN$. [d] CF in $CF_2CF(CF_3)CN$.

lation, was free of C≡N absorption in the infrared; the product from the bis(cyanoperfluoroalkyl)triazine could not be distilled because of its polymeric nature but had apparently undergone about 50% reaction. Irradiation of the latter product resulted in decreased ultraviolet absorption at 381 mμ and altered infrared absorption in the 600–1300-cm^{-1} region; these changes would be expected on elimination of nitrogen and coupling of the triazinobis(perfluoroalkyl) radicals so formed. Physical constants of the various triazine derivatives are given in Table II, and nmr spectral data in Table III.

Experimental Section

Preparation of $CF_2ClCFClCF_2COOC_2H_5$.—Into a stainless-steel pressure vessel were loaded 57.5 ml of $CF_2ClCFClCF_2CFCl_2$ (3M Kel-F Dimer No. 464), 55 ml of concentrated sulfuric acid, and 26.5 ml of 30% oleum. The vessel was heated and rocked for 48 hr at 200°. Distillation of the product gave 127 g of crude acid [bp 61° (1 mm)] containing large amounts of sulfur trioxide and other impurities. Some unreacted Kel-F dimer was usually recovered.

The crude acid (50 g) was added dropwise to 40 ml of absolute ethanol stirred and cooled in a water bath. When addition was complete the mixture was heated to 100°, evolving large quantities of acidic gases, then cooled and drowned in ice water. The organic layer was separated, washed, dried, and distilled, giving The over-all conversion to ester, based on unrecovered Kel-F dimer, averaged about 45% for 25 runs.

Preparation of $CF_2ClCFClCF_2CONH_2$.—A solution of 48 g of $CF_2ClCFClCF_2COOC_2H_5$ (0.17 mole) in 20 ml of 95% ethanol was stirred and cooled in an ice bath while ammonia gas was slowly bubbled through for 4 hr. Solvents excess ammonia were removed by heating gradually to 75° at 10 mm. The crystalline mass which formed on cooling was dissolved in hot cyclohexane, filtered if the solution was turbid, and recrystallized. The yield was 42 g of amide, mp 73°, or 98%.

Preparation of $CF_2ClCFClCN$.—Finely ground $CF_2ClCFClCF_2CONH_2$ (40 g, 0.16 mole) was mixed with about 80 g of phosphorus pentoxide and slowly heated to 200° over a period of 5 hr in an evacuated flask attached to a large trap cooled in Dry Ice–acetone. The resulting nitrile (36 g, 97% of theory) was 99.5% pure by chromatographic analysis and boiled at 67° (630 mm).

Preparation of Perfluoro[2,4-bis(2,3-dichloropropyl)]-6-alkyltriazines.—The 6-perfluoropropyl compound was made as follows. For the 6-trifluoromethyl compound trifluoroacetic anhydride was substituted for $(C_3F_7CO)_2O$.

Dry ammonia (3.35 g, 0.197 mole) was measured accurately by use of a calibrated gas volume in a vacuum system and transferred into a solution of 90 g (0.39 mole) of $CF_2ClCFClCF_2CN$ in 50 ml of ether, cooled to −100° or below. A stopcock on the reaction flask was closed and the contents warmed slowly with constant swirling until a temperature of 0° had been reached and no further exotherm was apparent, then left in an ice bath to warm to room temperature overnight. The resultant imidoylamidine solution was filtered and added dropwise to 400 g (*ca.* 1 mole) of $(CF_3CF_2CF_2CO)_2O$ stirred at 0 ± 5°. The mixture was then stirred for 3 hr while warming to room temperature. Solvent and excess acids were distilled off at 50 mm and the residue was fractionated through a short vacuum-jacketed Vigreux column to give 118 g of product, or 93% of theory.

Anal. Calcd for $C_{12}Cl_4F_{17}N_3$: C, 22.1; F, 49.7; N, 6.5. Found: C, 22.2; F, 50.3; N, 5.8.

Nmr.—The spectrum of the 6-CF_3 compound showed peaks at δ values of (A) 63.7 (CF_2Cl), (B) 73.2 (CF_3), (C) 111 ($\mathit{CF_2}$-CFCl), and (D) 132 ppm (CFCl). The areas of the peaks represented, respectively, 4.3, 2.9, 4.0, and 2.0 fluorine atoms. The CF_2Cl peak was a quadruplet showing coupling constants of 10.4 (A–C) and 9.4 cps (A–D). The CFCl peak was a quintuplet with coupling constants of 9.4 (A–D) and 5.3 cps (C, D). The CF_3 peak was a singlet and the $\mathit{CF_2}$CFCl peak a multiplet.

Preparation of Perfluoro(2,4-diallyl-6-alkyl)-*s*-triazines. A. Dehalogenation in Vapor Phase.—A 0.5-in.-i.d. nickel tube was packed with steel wool and heated in a vertical tube furnace over a 12-in. length to the desired temperature, with continuous nitrogen flush. Perfluoro[2,4-bis(2,3-dichloropropyl)]-6-methyl-*s*-triazine (3 g) was then added dropwise over 30 min. The product collecting at the bottom of the tube was subjected to chromatographic analysis, with the results given in Table I, p 2237.

B. Dehalogenation in Solution.—A mixture of 15 g (0.03 mole) of perfluoro[2,4-bis(2,3-dichloropropyl)]-6-propyl-*s*-triazine, 9.0 g (0.14 g-atom) of zinc, and 0.2 g of anhydrous zinc chloride was stirred at reflux in 30 ml of dioxane for 5 hr. The zinc had previously been activated by bringing it to reaction in dilute hydrochloric acid and washing it repeatedly with water and acetone, and ether. The dark reaction mixture was cooled, filtered, the solvent was removed at 100 mm, and the residue was distilled to give 9.0 g of C_3F_7 diallyltriazine (77% yield). Larger runs gave generally similar results.

Anal. Calcd for $C_{12}F_{17}N_3$: C, 28.3; F, 63.5; N, 8.2. Found: C, 28.8; F, 62.7; N, 8.7.

Nmr.—Only four peaks were found, rather than the expected five, for the 6-CF_3 compound, as the peak due to the α-CF_2 was apparently superimposed on one-half of the doublet due to the terminal CF_2 fluorine. Chemical shifts and relative areas were as follows: CF_3 71.5 ppm, 3.0; one-half of the terminal CF_2 90 ppm, 2.1; α-CF_2 plus one-half of the terminal CF_2 105 ppm, 5.8; CF 167 ppm, 2.1. Coupling constants of the terminal CF_2 fluorine were J_{gem} = 84 cps, with CF, J_{cis} = 5.1 cps, and J_{trans} = 11.7 cps.

Photochemical Reaction of Perfluoroglutaryl fluoride with Perfluorodiallyltriazines.—The acid fluoride was made in good yield by heating perfluoroglutaryl chloride with anhydrous potassium fluoride in diethyl carbitol under a short distilling column. Fractionation of the distillate obtained below a head temperature of 50° gave the acid fluoride [bp 41.5° (630 mm)] showing only COF and no COCl infrared absorption.

In a Vycor tube previously flushed with nitrogen, shielded over most of the vapor zone, and equipped with reflux condenser and Dry Ice trap, 6.0 g (0.012 mole) of C_3F_7 diallyltriazine and 3.0 g (0.012 mole) of $CF_2(CF_2COF)_2$ were stirred magnetically and irradiated with a Shannon 250-w lamp for 9 days. A solid film appeared on the tube walls nearest the lamp in 4 days or less. Distillation gave 3.0 g of unreacted triazine and 1.5 g of material which boiled at 30–150° (30–50 μ). An infrared spectrum of this liquid showed triazine, acid fluoride, and C=C absorption. The film was extracted successively with tetrahydrofuran, Freon 113, and acetone, dissolving in none of these at room temperature. After this treatment, it gave an infrared spectrum which, although poorly defined, was similar to that of the liquid except that the COF band had been replaced by COOH, probably because of hydrolysis by moisture in the solvents.

The Addition of Mercuric Fluoride to Perfluoroallyltriazines. A. Perfluoro-2,2-bis[2-(2,3-dichloropropyl)-4 propyltriazine]diisopropylmercury.—A small stainless-steel pressure vessel was flushed with nitrogen, cooled in an ice bath, and 23 g (0.04 mole) of perfluoro[2-allyl-4-(2,3-dichloropropyl)]-6-propyl-*s*-triazine, 5.8 g (0.024 mole, 20% excess) of mercuric fluoride, and 30 ml of anhydrous hydrogen fluoride were added. The bomb was sealed and oscillated at 90–100° for 10 hr, then cooled slightly, and vented. The crude product was extracted with three 20-ml portions of methylene chloride, the extract was treated with sodium fluoride, and the solvent was removed. Distillation of the residue gave 16 g of a viscous, colorless liquid [bp 155–160° (50–100 μ)] or 57% of theory. The product crystallized in the receiver and melted slightly above room temperature. An infrared spectrum showed the usual triazine and CF bands but no C=C absorption, and a qualitative test for mercury was strongly positive.

B. Poly[perfluoro-2-alkyl-4-(2-methyl-2-mercuriethyl)-6-(2-methylethylene)]-*s*-triazine.—The same vessel was loaded with 29 g (0.071 mole) of perfluoro(2,4-diallyl-6-methyl)-*s*-triazine, 17 g (0.071 mole) of mercuric fluoride, and 35 g of hydrogen fluoride, sealed, and oscillated at 100° for 21 hr. It was cooled slightly and vented; then vacuum was applied cautiously and increased slowly, finally being left at full water pump vacuum for 0.5 hr or so. If the mercurial was to be used for preparation of a diiodide, it was not further treated before adding iodine and FC-75. Separation of the polymer from the very corrosive and hygroscopic hydrogen fluoride was difficult without some damage to the triazine structure, as indicated by the appearance of infrared absorption near 6 μ; however, the triazine band remained strong and no C=C absorption appeared in the product spectrum when equimolar amounts of mercuric fluoride and perfluorodiallyltriazine were used.

Preparation of Iodoperfluoroalkyltriazines.—The crude polymeric mercurial from 29 g (0.07 mole) of perfluoro(2,4-diallyl-6-6-methyl)-*s*-triazine reacted in a pressure vessel with 30 g (0.12 g-atom) of iodine and 10 ml of 3M solvent FC-75 for 24 hr at 120°. The bomb was cooled, opened, and decanted; the residue of mercuric iodide and iodine was washed with additional FC-75. Solvent removal and distillation gave 29 g of product [bp 55–58° (40 μ)] or 58% of theory.

Anal. Calcd for $C_{10}F_{15}I_2N_3$: C, 17.0; I, 36.0; N, 6.0. Found: C, 17.9; I, 38.1; N, 6.4.

Nmr.—Sterically hindered rotation of the α-CF_2 group due to the large iodine atom caused nonequivalence of these two fluorine atoms, which consequently appeared as two quintuplets, rather than as a split doublet. Chemical shifts and relative peak areas were (A) CF_3 71.6 ppm, 2.7; (B) CF_3CF 72.6 ppm, 5.8; (C, D) CF_2 103.1 ppm, 4.1; (E) CF 143.5 ppm, 2.0. Peak A was a singlet, B was a quadruplet because of nonequivalence of C and D, C and D were quintuplets with J_{gem} = 29 cps, and E was a quintuplet.

Coupling of Perfluoro-2-[(2,3-dichloropropyl)-4-(2-iodopropyl)-6-propyl]-*s*-triazine.—In a 25-ml Pyrex flask illuminated by a Shannon ultraviolet lamp at a 2-in. distance, 8.5 g of the above compound, 15.0 g of mercury, and 10 ml of FC-75 were stirred under a reflux condenser for 6 hr. The crude product was filtered, the solvent was removed, and the residue was distilled *in vacuo*, giving 5.8 g of colorless, very viscous liquid, or 83% yield. The distillate gave an infrared spectrum very similar to that of perfluoro[2,4-bis(2,3-dichloropropyl)]-6-propyl-*s*-triazine.

Anal. Calcd for $C_{24}F_{35}N_6$: mol wt, 1199. Found: mol wt (ebullioscopic in benzene), 1091.

Preparation of Perfluoroalkylcyanotriazines.—A solution of 24.4 g (0.056 mole) of 2,4-bis(perfluoroisopropyl)-6 fluoro-*s*-triazine in 25 ml of dry acetonitrile, cooled to 0°, was treated with 3.0 g (0.062 mole) of powdered sodium cyanide in small portions over a period of 30 min. The mixture was stirred at 0° for 5.5 hr, warmed to room temperature, and filtered under nitrogen. Distillation through a vacuum-jacketed Vigreux column, after removal of solvent, gave 20.2 g (82%) of product, bp 67° (10 mm).

Dry ammonia (7 mmoles) was transferred at liquid nitrogen temperature into a solution of 5.0 g of perfluorosuberonitrile (14 mmoles) in 15 ml of dry ether. The mixture was allowed to warm to 0° over 20 min, then left in an ice bath overnight. The colorless, clear solution was added to 20.0 g of trifluoroacetic anhydride and cooled in a Dry Ice–acetone bath; the mixture was stirred as the temperature rose from −10 to 25° over 3 hr. Solvents were removed and the residue was distilled to give 2.8 g [bp 105–106° (1 mm)], or 44% yield.

Anal. With the exception of the nitrogen values, elementary analytical results for the perfluoroalkylcyanotriazines were unsatisfactory; however, the structures were established by infrared and nmr spectra. The former showed absorptions for triazine ring, cyano group, and carbon–fluorine, while the latter showed correct area ratios and reasonable δ values for the various fluorine-containing groups, as given in Table III.

Reaction of Cyanoperfluoroalkyltriazines and Perfluoroalkylcyanotriazines with Silver Difluoride.—2,4-Bis(perfluoroisopropyl)-6-cyano-*s*-triazine (7 g, 0.016 mole) and 6.5 g (0.044 mole) of silver difluoride heated for 12 hr at 130°, after extraction and solvent removal, gave 6.9 g of a mixture which on infrared examination proved to be a 1:1 mixture of the 6-cyanotriazine and 2,4-bis(perfluoroisopropyl)-6-fluoro-*s*-triazine.

Perfluoro[2,4-bis(6-cyanohexyl)-6-methyl]-*s*-triazine (2.5 g, 31 mmoles) and 3.8 g (260 mmoles) of silver difluoride, heated in 10 ml of FC-75 for 18 hr at 100°, gave a yellow nonvolatile liquid after solvent removal.

Perfluoro[2,4-bis(6-cyanoisopropyl)-4,6-diisopropyl]-*s*-triazine (5 g) when heated at 125° for 18 hr with a 100% excess of silver difluoride in FC-75 gave on distillation 2.2 g of the starting triazine and 2.1 g (70%) of the presumed azo compound, bp 94–95° (70 μ).

The spectral properties of these materials are discussed in the text.

Registry No.—$CF_2ClCFClCF_2COOC_2H_5$, 648-08-8, $CF_2ClCFClCF_2CONH_2$, 10414-82-1; $CF_2ClCFClCN$; 421-96-5; perfluoroglutaryl fluoride, 678-78-4; mercuric fluoride, 7783-39-3; perfluoro-2,2-bis[2-(2,3-dichloropropyl)-4-propyltriazene]diisopropylmercury, 10408-00-1; silver difluoride, 7783-95-1.

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Studies on the Diazo-β-azomethine–*v*-triazine Equilibrium[1,2]

CARROLL TEMPLE, JR., C. L. KUSSNER, AND JOHN A. MONTGOMERY

Kettering-Meyer Laboratory, Southern Research Institute, Birmingham, Alabama 35205

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The nitrosation of some 3-[5- (or 4-) aminoimidazol-4- (or 5-) yl]-*s*-triazoles and 5-[5- (or 4-) aminoimidazol-4- (or 5-) yl]tetrazoles is described. The resulting diazoimidazole–*v*-triazine systems are used to study the effect of solvent and certain groups on the diazo-β-azomethine–*v*-triazine equilibrium. Structure assignments are based on data obtained from the infrared and proton magnetic resonance spectra.

The nitrosation of 5- (or 4-) aminoimidazole-4- (or 5-) carboxamide provided 5-diazoimidazole-4-carboxamide, which was readily converted to imidazo[4,5-*d*]-*v*-triazin-4(3H)-one (2-azahypoxanthine).[3a] Similarly 4-aminoimidazo[4,5-*d*]-*v*-triazine (2-azaadenine) was obtained directly from 5- (or 4-) aminoimidazole-4- (or 5-) carboxamidine.[4] Although other condensed *v*-triazines behave as the corresponding diazo isomers on reaction with nucleophiles,[5] the conversion of an imidazo[4,5-*d*]-*v*-triazine to a diazoimidazole is unreported.[6] In this paper the preparation of some diazoimidazole–*v*-triazine systems, and the effect of solvent and certain groups on the diazo-β-azomethine–*v*-triazine equilibrium is described.

6-(1-Benzylhydrazino)purine (**1**), prepared from 6-chloropurine and benzylhydrazine, was treated with diethoxymethyl acetate to give a mixture of **2** and **3** that was resolved. The latter (**3**) results from opening of the pyrimidine ring of **2** during the reaction.[7a] Treatment of either **2** or **3** with 11% methanolic hydrogen chloride provided the aminoimidazole **4**. Similarly, treatment of 9-benzyl-6-hydrazinopurine with phosgene resulted in cyclization and opening of the pyrimidine ring to give directly 5-(5-amino-1-benzylimidazol-4-yl)-*s*-triazol-3-ol (**12**). The preparation of the remaining aminoimidazoles (**5**, **10**, **11**, **14**, **15**, and **16**) has been reported.[7] The nitrosation reaction was carried out by the addition of sodium nitrite to a solution of the aminoimidazole in hydrochloric acid with the exception of **5**, which gave unidentified products by this method. A pure product was obtained, however, by the addition of the dihydrochloride of **5** to a solution of sodium nitrite. Although system **17** was prepared successfully on a small scale, the dried product from a large run exploded violently (see the Experimental Section). The properties of the new compounds are summarized in Table I.

Results and Discussion

The structure assignments, based on the infrared and proton magnetic resonance (pmr) spectra of solutions of the diazoimidazole–*v*-triazine systems, are presented in Table II. In the nitrosation of **5** two crops with identical ultraviolet spectra but different infrared spectra were obtained. In the first crop the presence of a strong diazo band at 2170 cm^{-1} and of only weak bands in the 1700–1500-cm^{-1} region of the infrared spectrum indicated that this material was mainly 3-[5- (or 4-) diazoimidazol-4- (or 5-) yl]-*s*-triazole (**6a**) (see Scheme I).[8] In contrast, the infrared spectrum of the second solid exhibited bands at 2145, 1670, and 1640 cm^{-1} indicating that this material was a mixture of **6a** and an isomeric *v*-triazine form, either **6b** or **6c**. The greater nucleophilicity of N-1 over N-4 of the *s*-triazole ring has been demonstrated by the cyclization of **5** with formamide to give *s*-triazolo[5,1-*i*]purine.[7] The cyclization to N-1 rather than N-4 has also been observed in other *s*-triazolo compounds.[9] Thus, the cyclization of **6a** should give mainly **6c** rather than **6b**. Additional evidence that ring closure to N-1 is favored over N-4 is provided by the preparation of **7a** (see below).

No significant change occurred in the solid-state infrared spectral of the two crops described above over a period of 2 months. Both solids, however, coupled with 2-naphthol in glacial acetic acid to give good yields of the same naphthylazoimidazole (*via* **6a**). In contrast, the infrared spectrum of the sodium salt of **6** was transparent in the diazo absorption region, and showed bands at 1685 and 1640 cm^{-1}, indicating that this solid exists as the sodium salt of **6c**. Furthermore, neutralization of an aqueous solution of the salt deposited a mixture containing mainly **6a**.

In a trifluoroacetic acid (CF$_3$COOH) solution of **6** only one form was detected by the pmr spectrum. That this form is the diazo compound **6a** (protonated) was established by the presence of a strong diazo band at 2235 cm^{-1} in the infrared spectrum of the solution

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