The Preparation and Coupling of Some α-Haloperfluoromethyl-s-triazines[1]

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A variety of α-haloperfluoromethyl-s-triazines was used in a study of mercury-induced coupling reactions. Qualitatively, the order of reactivity of the α-halo atom is Br > Cl > F. α-Bromo is sufficiently reactive to allow the preparation of a linear poly(perfluoroalkylperfluoroalkylene-s-triazine) from 2,4-bis(bromodifluoromethyl)-6-trifluoromethyl-1,3,5-triazine. The new nitriles, CF_2BrCN and CF_2ICN, and the new anhydride, $(CF_2BrCO)_2O$, were prepared *via* specially developed routes. From these, several new substituted triazines were obtained by modification of available techniques.

Poly(perfluoroalkylenetriazines) were first prepared by Brown[2] by thermal deammonation of perfluoroalkyleneamidines.[3] The resulting polymers were of interest owing to their high degree of thermal and chemical stability. However, the random nature of the formation of the triazine ring precluded any great degree of linearity in the polymer structure. More recently, Dorfman, *et al.*,[4] described a procedure in which a poly(imidoylamidine) was first formed from an α,ω-fluorocarbon dinitrile followed by acylation and ring closure using a fluorocarbon acid anhydride to give the triazine structure. A much greater degree of polymer linearity was achieved.

To avoid uncontrolled triazine formation and rearrangement during condensation polymerization, and the undesirable cross-linking that resulted, it seemed advantageous to prepare and isolate pure samples of difunctional triazine compounds which could be coupled to a linear high polymer under conditions that would not affect the preformed triazine ring. Consequently, various α-halomethyltriazines (I) were prepared and their coupling reactions were studied using mercury as the coupling agent.

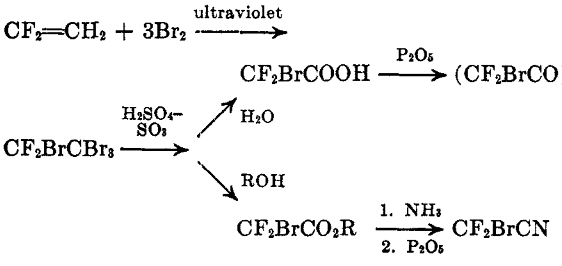
Results and Discussion

Precursors.—The synthesis of compound I required the preparation of the three nitriles, ClF_2CCN, BrF_2CCN, and IF_2CCN, and the anhydride, $(BrCF_2CO)_2O$. Chlorodifluoroacetonitrile was prepared from $CClF_2CONH_2$ as described previously.[5] Bromodifluoroacetonitrile was synthesized by two different routes.

$$CF_2{=}CF{-}CF{=}CF_2 + Br_2 \longrightarrow$$

$$CF_2BrCF{=}CFCF_2Br \xrightarrow[2.\ H^+\text{-}Et_2O]{1.\ KMnO_4} 2CF_2BrCOOH \xrightarrow{H^+\text{-}EtOH}$$

$$2CF_2BrCO_2Et \xrightarrow{NH_3} 2CF_2BrCONH_2 \xrightarrow{P_2O_5} 2CF_2BrCN \qquad (A)$$



$$CF_2{=}CH_2 + 3Br_2 \xrightarrow{\text{ultraviolet}} CF_2BrCBr_3 \xrightarrow{H_2SO_4\text{-}SO_3}$$

$$\xrightarrow{H_2O} CF_2BrCOOH \xrightarrow{P_2O_5} (CF_2BrCO)_2O$$

$$\xrightarrow{ROH} CF_2BrCO_2R \xrightarrow[2.\ P_2O_5]{1.\ NH_3} CF_2BrCN$$

(B)

Initially the bromodifluoroacetic acid used in this work was prepared according to route A. However, the cost of the starting material and the necessity of the permanganate oxidation step encouraged a search for a better route. Route B was readily adaptable to the production of large quantities of $CF_2BrCOOH$ or CF_2BrCO_2R, which served as precursors to $(CF_2BrCO)_2O$ and CF_2BrCN, respectively.

Iododifluoroacetonitrile proved to be more difficult to prepare.

$$CF_2Br_2 + F_2C{=}CH_2 \xrightarrow{\text{peroxide}} CF_2BrCH_2CF_2Br \xrightarrow{NaOH}$$

$$CF_2BrCH{=}CF_2 \xrightarrow{NaI} CF_2ICH{=}CF_2 \xrightarrow[2.\ EtOH]{1.\ KMnO_4}$$

$$CF_2ICOOEt \xrightarrow{NH_3} CF_2ICONH_2 \xrightarrow{P_2O_5} CF_2ICN$$

Oxidation of an acetone solution of $CF_2ICH{=}CF_2$, using neutral, aqueous $KMnO_4$ followed by esterification yielded the new compound, CF_2ICO_2Et. Decomposition of the ester during distillation, as indicated by the formation of large quantities of I_2, was thought to be one major cause of the low yield of product (20.6%). The ester was converted to CF_2ICONH_2 in good yield; treatment of this product with P_2O_5 at temperatures barely sufficient to initiate dehydration afforded an 83% yield of pure nitrile, CF_2ICN.

Triazine Syntheses.—The first perhalomethyl-s-triazine, tris(trichloromethyl)-1,3,5-triazine, was prepared by Dachlauer,[6] *via* trimerization of CCl_3CN using anhydrous HCl. The first fluorine-containing perhaloalkyl-s-triazines were synthesized by McBee, Pierce, and Bolt[7] by fluorination of the trimeric CCl_3CN with SbF_3. The triazines used in this investigation were prepared by the method of Brown[8] because of its versatility.

During this study the scope of this reaction was extended to include halodifluoroacetonitriles and halodifluoroacetic anhydrides (Scheme I).

Thus Ia was synthesized using CF_2BrCN in step I, CF_3CN in step II, and $(CF_3CO)_2O$ in step III. The versatility of the reaction sequence is shown by the fact that Ia was also synthesized using 2 equiv of CF_3CN in step I (thus bypassing step II) and $(CF_2BrCO)_2O$ in step III. Generally, triazines containing two or more identical groups were synthesized by by-

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[1] (a) This work was performed under Contract AF 33(615)-1233, Elastomer and Coatings Branch, Air Force Base, Ohio 45433. (b) For convenience the prefix halo includes only chlorine, bromine, and iodine.

[2] H. C. Brown, Abstracts of the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept 1955; the 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1958; and the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964.

[3] D. R. Husted, U. S. Patent 2,676,985 (1954).

[4] E. Dorfman, *et al.*, 89th National Meeting of the Division of Rubber Chemistry of the American Chemical Society, San Francisco, Calif., spring 1966.

[5] N. N. Yaroveneso, *et al.*, *Zh. Obshch. Khim.*, **27**, 2301 (1957).

[6] Dachlauer, German Patent 699,493 (Oct 31, 1940).

[7] E. T. McBee, O. R. Pierce, and R. O. Bolt, *Ind. Eng. Chem.*, **39**, 391 (1947).

[8] P. D. Schuman, Doctoral Thesis, University of Florida, Aug 1962.

TABLE I

PREPARATION OF I

Compd	Procedure	Starting materials Step I	Step II	Step III	Triazine distribution, glpc area %	Yield, %
Ia	B	$2CF_3CN$	...	$(CF_2BrCO)_2O$	Ia >90; Id, trace[a]	14.5
	A	CF_2BrCN	CF_3CN	$(CF_3CO)_2O$	Ia, 77.5; Ib, 8.1; Id, 14.4	51
Ib	B	$2CF_2BrCN$	...	$(CF_3CO)_2O$	Ib, 80.6; Ie, 19.4	74
Ic	A	CF_2ClCN	CF_2ClCN	$(CF_3CO)_2O$	Ic, 61[b]	28
Id	A	CF_3CN	CF_3CN	$(CF_3CO)_2O$	Id, 96	31
Ie	B	$2CF_2BrCN$	...	$(CF_2BrCO)_2O$	Ie[c]	15.8
If	B	$2CF_2ICN$	...	$(CF_3CO)_2O$	If, ~90	...

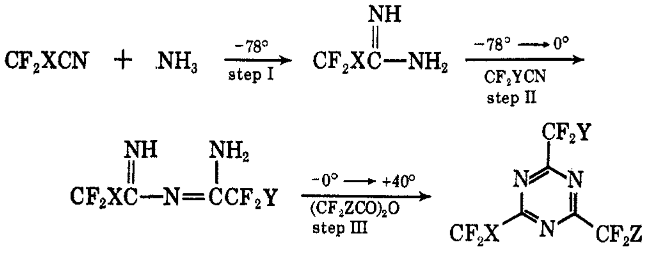
[a] Approximate data. [b] 2,4,6-Tris(chlorodifluoromethyl)-1,3,5-triazine = 39%. [c] No reliable glpc data available.

TABLE II

PHYSICAL CONSTANTS AND ANALYSES OF NEW COMPOUNDS

Compd	Bp, °C (mm)	$n^{25}D$	d^{25}_4	C, % Calcd	C, % Found	F, % Calcd	F, % Found	N, % Calcd	N, % Found	Halogen, % Calcd	Halogen, % Found
Ia	130	1.3718	1.804	20.83	21.2	43.91	45.0	12.15	11.40	23.10	...
Ib	82 (28)	1.4200	2.015	17.71	18.13	32.68	33.0	10.33	10.12	39.28	39.53
Ie	112.5 (25)	1.4632	2.16	15.40	15.52	24.37	...	8.98	8.90	51.25	50.4
CF_2ICO_2Et	144–145	1.4373	...	19.22	19.25	15.20	14.9	...	...	50.76	50.70
CF_2ICONH_2	Mp 99–99.5	...	...	10.81	11.7	17.20	...	6.34	6.19	57.44	56.2
CF_2ICN	46–47	...	...	11.84	11.9	18.72	...	6.90	6.57	62.54	...
$(CF_2BrCO)_2O$	121.8–124	1.3912	...	14.48	...	22.90	23.1	...	...	48.16	...
CF_2BrCN	3–5	...	...	15.40	...	24.37	24.0	8.98	...	51.25	...

SCHEME I



Ia, X = Br; Y = F; Z = F
X = F; Y = F; Z = Br
b, X = Br; Y = Br; Z = F
c, X = Cl; Y = Cl; Z = F
d, X = F; Y = F; Z = F
e, X = Br; Y = Br; Z = Br
f, X = I; Y = I; Z = F

passing step II. For example, Ie was synthesized using 2 equiv of CF_2BrCN in step I and $(CF_2BrCO)_2O$ in step III.

The product distributions and yields of these reactions are listed in Table I. New compounds are described in Table II. Notice that the desired triazine is obtained as the major product in each case, but varying yields of other triazines are also obtained. For example, 2,4,6-tris(chlorodifluoromethyl)-1,3,5-triazine was not sought directly but obtained as a byproduct in the preparation of Ic. The presence of other triazines can be rationalized by the following system of equilibria, using the preparation of Ia as an example. The intended route is shown with heavy arrows (Scheme II).

The presence of Ie found in the preparation of Ib is more difficult to explain but could be due to a simple trimerization of CF_2BrCN. All the products of this reaction could also be accounted for by assuming a catalytic ring cleavage of Ia and a random shuffling of two groups between three sites. Such a catalyst was not sought.

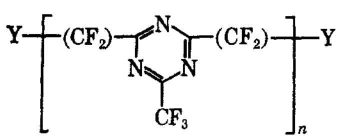
Coupling Studies.—It has been found that α-bromoperfluoromethyl-s-triazines display an unusually high degree of reactivity toward coupling in the presence of mercury at elevated temperatures. For example, 2-bromodifluoromethyl-4,6-bis(trifluoromethyl)-1,3,5-triazine (Ia) underwent intermolecular debromination to yield 1,2-di[4,6-bis(trifluoromethyl)-1,3,5-triazinyl]-tetrafluoroethane (IIa, Scheme III). Furthermore, the difunctional triazine, 2,4-bis(bromodifluoromethyl)-6-trifluoromethyl-1,3,5-triazine (Ib), underwent varying degrees of coupling, depending upon reaction conditions, to give linear polymeric chains ranging from a dimeric species to a chain of approximately 350 units (IIb). For example, at a temperature of 160° for several hours Ib yielded mainly a linear dimer, trimer, and tetramer which were isolated and characterized. At higher temperatures or for a longer reaction period high polymers, with an average $n \geq 350$, were formed. The molecular weight of the polymer obtained was calculated from end-group analysis data, assuming a bromine-terminated polymer. The validity of this assumption is supported by the following data. (1) Low polymer (n = 35–40), as well as pure dimer (n = 2), could be further coupled to high polymer, showing that coupled products are still difunctional. (2) Elemental analyses of pure dimer, trimer, and tetramer support a perfluoroalkylperfluoroalkylenetriazine structure in which this functionality is still the C–Br bond. (3) No macrocyclic compounds have been detected among the isolable, low molecular weight species. The coupled products are described in Table III.

The corresponding chloro compound, 2,4-bis(chlorodifluoromethyl)-6-trifluoromethyl-1,3,5-triazine (Ic), on the other hand was relatively inert in the presence of mercury. At 300° for 16 hr, Ic gave a small amount of a product which was not isolated, but rather detected by glpc and assumed to be IIc (n = 2, the balance of the material).

The completely fluorinated analog, 2,4,6-tris(trifluoromethyl)-1,3,5-triazine (Id), was completely inert to mercury at 250° for 16 hr. Indeed, it is this inertness of the CF_3 group that allows the formation of only dimer from Ia, and linear polymer from Ib.

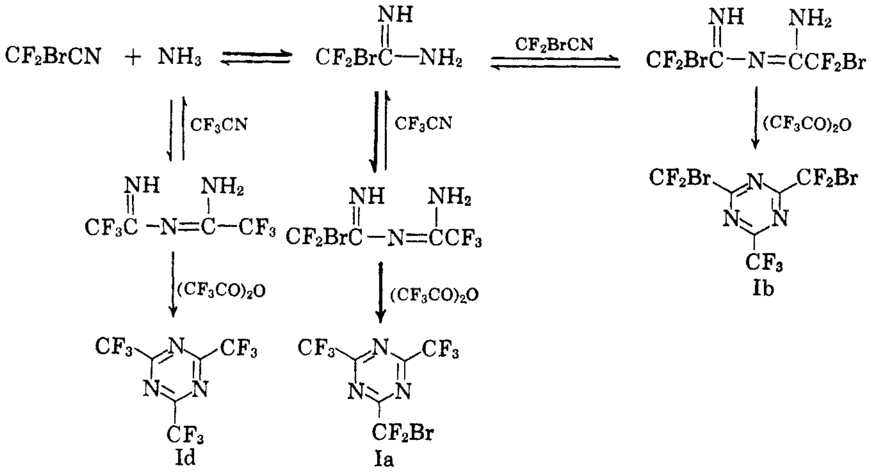
Table III

Preparation of II

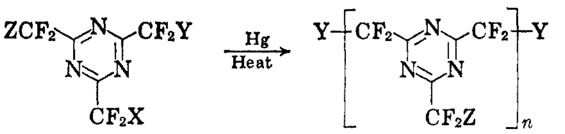


Product	Y	n	Mp, °C	C, % Calcd	C, % Found	N, % Calcd	N, % Found	Br, % Calcd	Br, % Found
IIa	F	2	41.5	27.08	27.3	15.79	15.1	...	...
IIb (dimer)	Br	2	35.5–36	22.04	22.3	12.85	12.1	24.44	...
IIb (trimer)	Br	3	70–72	23.99	24.8	13.99	13.3	17.74	...
IIb (tetramer)	Br	4	89–90	25.11	26.3	14.64	14.1	13.92	...
IIb (prepolymer)	Br	3–4	114–117	23.99–25.11	24.4	13.99–14.64	...	17.74–13.92	16.2, 15.6
IIb (low polymer)	Br	35–40	135–138	28.64–28.70	...	16.70–16.74	...	1.81–1.59	1.56–1.64
IIb (high polymer)	Br	350	>350	29.11	27.7	16.97	16.4	0.18	<0.20

Scheme II



Scheme III



Ia-d

IIa, $n = 2$; Y = F; Z = F
b, $n = 1$-350; Y = Br; Z = F
c, $n = 1(2)$; Y = Cl; Z = F
d, $n = 1$ only; Y = F; Z = F

Experimental Section

All boiling points and melting points are uncorrected. Melting points were determined on a Fisher-Johns melting point apparatus. Gas phase chromatography was conducted on an F & M Model 720 using a 10 ft × 0.25 in. column containing 20% FS 1265 fluid, 10,000 centistokes on Anakrom 90–100 mesh ABS. Infrared spectra were obtained with a Perkin-Elmer Model 137 Infracord.

CF_2BrCH_2Br.—Vinylidene fluoride was bubbled rapidly into 2981 g of bromine at ambient temperature, in the presence of an 8-w ultraviolet source until the color of bromine was discharged. The light yellow liquid (4138 g, 99%) was used without purification, bp 93.2°, $n^{25}D$ 1.4434 (lit.[9] bp 92.8°, $n^{20}D$ 1.4456).

CF_2BrCBr_3.—In the presence of a 250-w ultraviolet source (G.E. Model UA-2) 450 g of CF_2BrCH_2Br was refluxed and treated with 700 g of bromine at such a rate as to keep the reaction temperature above 90°. After 48 hr, the reaction mixture was distilled to remove volatile material, leaving 640 g (83.5%) of CF_2BrCBr_3 in the flask, mp 99–100° (lit.[10] mp 99°).

CF_2BrCO_2Et.—A mixture of 1029 g of CF_2BrCBr_3, 65 g of $HgSO_4$, and 10 g of Hg_2SO_4 was heated to 100° and treated with 400 ml of 30% fuming H_2SO_4 over a period of 2 hr. The reaction mixture was stirred at reflux (bromine is produced) overnight, cooled, and distilled to remove volatile material (pot temperature, 120°). The cooled residue was filtered through a fritted glass funnel to remove the mercury salts; the filtrate was added cautiously to cold (0°) ethanol and the final solution was stirred at room temperature for 16 hr. The reaction mixture was quenched with an equal volume of iced water, and the insoluble liquid, (393 g) was separated, dried with "Drierite," and fractionated to give 329 g (60.5%) of CF_2BrCO_2Et, bp 115–115.5°, $n^{25}D$ 1.3890 [lit.[11] bp 112° (700 mm), $n^{25}D$ 1.3900].

$CF_2BrCOOH$.—Tetrabromodifluoroethane (1322 g) was treated with 275 ml of 65% fuming H_2SO_4 as described above, excluding the esterification reaction, and the resulting filtrate was treated with excess water. The organic phase was separated and the aqueous phase was extracted with ether. Fractionation of the combined phases yielded 362 g (61%) of $CF_2BrCOOH$, bp 49° (14 mm) (lit.[12] bp 145–160°).

Reactions Using Perfluorobutadiene.—Perfluorobutadiene (98.6 g) was condensed into a flask with the aid of a Dry Ice–acetone bath and was treated with 98.6 g of Br_2 by drops. A ultraviolet source (G.E. Model UA-2) was needed to effect bromination. The product was decolorized with aqueous $NaHSO_3$, washed with water, and dried over $CaCl_2$. The colorless liquid (180.5 g, 93%) was shown by glpc to consist of two closely boiling compounds (probably *cis* and *trans* isomers) that were present in a ratio of 6.5:1. The product was oxidized without further purification, using a slurry of 118 g of $KMnO_4$ and 133 g of $NaHCO_3$ in 500 ml of H_2O. Dibromohexafluorobutene was added to the cold oxidizing solution at such a rate as to keep the reaction temperature below 15°. The mixture was cautiously acidified with 200 ml of 1:1 aqueous H_2SO_4 and then treated with SO_2. Starting material (17 g) was removed by separation and the aqueous phase was extracted continuously with ether for 104 hr. The dried ethereal solution of bromo-

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(9) A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **70**, 1025 (1948).

(10) P. Tarrant, A. M. Lovelace, and M. R. Lilyquist, *ibid.*, **77**, 2783 (1955).

(11) H. Cohn and E. D. Bergmann, *Israel J. Chem.*, **2**, 355 (1965).

(12) F. Swarts, *Bull. Soc. Chim. France*, 597 (1903).

difluoroacetic acid was treated with a solution of 121 g of concentrated H_2SO_4 in 115 g of ethanol (cautiously prepared at 5–10°) at ambient temperature and the final solution was refluxed for 23 hr. The reaction was quenched with 400 ml of H_2O and the ether phase was separated, washed, and dried with anhydrous $CaSO_4$. Treatment of this solution of ethyl bromodifluoroacetate with excess NH_3, followed by removing the solvent and recrystallizing the solid from benzene, gave 94 g (55%) based on perfluorobutadiene) of bromodifluoroacetamide, mp 81–82.5° (lit.[11] mp 86.5–87°).

$(CF_2BrCO)_2O$.—Bromodifluoroacetic acid (350 g) was slurried with 400 g of P_2O_5 and the mixture was gradually heated to 300°. The volatile material which distilled from the flask was condensed and fractionated to give 185 g (56%) of $(CF_2BrCO)_2O$ (Table II). The infrared spectrum of this material showed strong absorptions at 5.38, 5.59, and 5.62 and a slight peak at 3.35 μ.

$CF_2BrCONH_2$.—Ethyl bromodifluoroacetate (475 g) was dissolved in an equal volume of ethyl ether and treated with anhydrous NH_3 until glpc showed the reaction to be complete. The solvent was removed with a rotary evaporator and the crude product (363 g, 89%) was recrystallized from hexane, mp 84.5–85.5 (lit.[11] mp 86.5–87°).

CF_2BrCN.—An intimate mixture of 229.3 g of $CF_2BrCONH_2$ and 567 g of P_2O_5 was gradually heated to 250°. The volatile material, 183.7 g (89%), was collected in a Dry Ice cooled trap (Table II). An infrared spectrum of the gas showed a strong absorption at 4.47 μ for the $C{\equiv}N$ group.

CF_2ICO_2Et.—1,1,3,3-Tetrafluoro-3-iodopropene was prepared by the method of Tarrant.[13,14] An 85% solution of 1,1,3,3-tetrafluoro-3-iodopropene in acetone (452 g) was slowly added to a mixture of 364 g of $KMnO_4$ and 1000 ml of water at 0–12°. The mixture was stirred for 1 hr at 0° after the addition was completed, acidified with 100 ml of concentrated H_2SO_4, and treated with gaseous SO_2 at such a rate as to maintain a temperature not greater than 12°. The aqueous phase was extracted with ether continuously for 72 hr. The ether phase was concentrated to 250 ml and treated with 150 g of absolute ethanol and 10 ml of concentrated H_2SO_4, and the solution was refluxed for 2 hr. The solution was cooled and quenched with water, and the ether phase was separated and dried. Fractionation of the product through an 18 × 0.5 in. vacuum-jacketed column packed with glass helices gave CF_2ICO_2Et, bp 37–42° (30 mm). The I_2 that was generated during this distillation was removed from the product with $Na_2S_2O_3$ solution. The washed and dried CF_2ICO_2Et was analyzed and used without further purification (Table II). An average yield of 20.6% was obtained for five runs.

CF_2ICONH_2.—Ammonia was bubbled into an ether solution of CF_2ICO_2Et (90 g in 200 ml of ether) for 2.5 hr. The progress of the reaction was monitored with glpc. Evaporation of the solvent yielded 76.9 g (97%) of a solid, mp 92–96°. Recrystallization from CCl_4 gave CF_2ICONH_2, mp 99–99.5° (Table II).

CF_2ICN.—An intimate mixture of 41.5 g of CF_2ICONH_2 and 101.5 g of P_2O_5 was placed in a foil-covered flask fitted with a Claisen head and gradually heated until CF_2ICN distilled from the apparatus. This temperature (approximately 100°) was maintained while 31.5 g (83%) of CF_2ICN distilled (Table II). An infrared spectrum showed an absorption at 4.48 μ for the $C{\equiv}N$ group.

Triazine Syntheses. General Comments.—All glassware was purged with purified nitrogen and heated to ensure dryness. The reactions were conducted under a dry atmosphere to prevent hydrolysis of the amidine or imidoylamidine intermediates. Two procedures were used to prepare triazines. In procedure A, step I (Scheme I) was accomplished by adding nitrile to ammonia, followed by step II. In procedure B, steps I and II were combined by adding ammonia to nitrile, thereby ensuring that imidoylamidine formed as soon as amidine was present. Step III was the same in both procedures.

2,4-Bis(trifluoromethyl)-6-bromodifluoromethyl-1,3,5-triazine (Ia). Procedure A.—A solution of 3.30 g of NH_3 in 100 ml of ether was cooled with a Dry Ice–acetone bath and treated with 26.6 g of CF_2BrCN. The cloudy solution of bromodifluoroacetamidine was then treated with excess CF_3CN. The clear solution of N′-bromodifluoroacetimidoyltrifluoroacetamidine was then warmed to 0° and treated with 105 g of $(CF_3CO)_2O$ dissolved in 100 ml of ether. The final solution was stirred for 10 hr at 25° and distilled to remove low-boiling materials, and the residue (127.5 g) was washed with water. The insoluble material (86.5 g) was fractionated on a 18 × 0.5 in. glass helices packed column, to give 15 g of Ia (51% of theory based on CF_2BrCN), bp 52–53° (31 mm). A capillary boiling point of 130° was observed at atmospheric pressure (Table II).

2,4-Bis(trifluoromethyl)-6-bromodifluoromethyl-1,3,5-triazine (Ia). Procedure B.—Trifluoroacetonitrile (23.4 g) was dissolved in 100 ml of CH_2Cl_2 at −78° and treated with 2.0 g of anhydrous ammonia. The temperature was allowed to increase to 0° over a 5-hr period. The clear solution of imidoylamidine was treated with 90 g of $(BrCF_2CO)_2O$ over a 15-min period and the resulting solution was warmed to 25°. The solution was then poured over ice and the insoluble layer was washed with three portions of water before being dried with $CaCl_2$. Distillation gave 13.4 g of a liquid, bp 123–130°, which was shown by glpc to be approximately 50% Ia. A small sample was separated by preparative glpc; its infrared spectrum was superimposable with that of Ia prepared by procedure A.

2,4-Bis(bromodifluoromethyl)-6-trifluoromethyl-1,3,5-triazine (Ib). Procedure B.—Methylene chloride (500 ml), 765 g of CF_2BrCN, and 41.7 g of NH_3 were used in step I, followed by 1080 g of $(CF_3CO)_2O$ in step III. The final solution was washed, dried, and fractionated to give 735 g of Ib (74%, Table II).

2,4-Bis(chlorodifluoromethyl)-6-trifluoromethyl-1,3,5-triazine (Ic). Procedure A.—Ammonia (21.9 g) was treated with 141 g of CF_2ClCN at −75°, then by another 141 g of CF_2ClCN at 0°, and 515 g of $(CF_3CO)_2O$, also at 0°. No solvent was used in this preparation; consequently during step I the reaction mixture became solid and stirring was not possible. During step II the reaction mixture became a slurry and stirring was again possible. The final, clear solution was heated at 80° for 1 hr, cooled, and poured over ice to destroy excess anhydride. The crude, insoluble product (185 g) was separated, washed, and dried with Drierite. Fractionation gave 87 g of Ic (21.6%), bp 145°, $n^{20}{}_D$ 1.3822 (lit.[7] bp 145°, $n^{20}{}_D$ 1.3827), and 58 g of 2,4,6-tris-(chlorodifluoromethyl)-1,3,5-triazine (20.6%), bp 170.5°, $n^{24}{}_D$ 1.4108 (lit.[7] bp 166.6–168.8°, $n^{20}{}_D$ 1.4129).

2,4,6-Tris(trifluoromethyl)-1,3,5-triazine (Id). Procedure A.—Ammonia (60 mmoles) was treated with 57.6 mmoles of CF_3CN by freezing the nitrile above the ammonia in an ampoule which was connected to a vacuum line and allowing the nitrile to melt and run down to the frozen ammonia. The resulting amidine was treated with 58.8 mmoles of CF_3CN at −78° and allowed to react at 25°. A portion (3.55 g) of the N′-trifluoroacetamidoyltrifluoroacetamidine was treated with 14.5 g of $(CF_3CO)_2O$ at 0° and the product was washed with water to yield 1.5 g (30.7%) of Id. Its infrared spectrum was identical with that of an authentic sample.[15]

2,4,6-Tris(bromodifluoromethyl)-1,3,5-triazine (Ie). Procedure B.—A solution of 70 g of CF_2BrCN in 40 ml of CH_2Cl_2 was cooled in an ice bath and treated with 3.2 g of NH_3. The clear solution was stirred at 0° for 0.5 hr and then treated with a solution of 185 g of $(CF_2BrCO)_2O$ in 60 ml of CH_2Cl_2. The final solution was distilled to remove volatile components and the residue was washed with water. The dried organic material was fractionated on a 6-in. Vigreux column to give 14 g of Ie (Table II).

2,4-Bis(iododifluoromethyl)-6-trifluoromethyl-1,3,5-triazine (If). Procedure B.—Iododifluoroacetonitrile (7.1 g) was treated with 0.35 g of NH_3 by freezing the reactants in an ampoule with liquid nitrogen and allowing the ampoule to warm to room temperature. The viscous liquid was frozen and treated with 11.5 g of $(CF_3CO)_2O$ in a similar fashion. The crude product was warmed to 25° and kept there for 2 days before being dissolved in CH_2Cl_2 and washed with a $Na_2S_2O_3$ solution to destroy I_2. The dried methylene chloride solution was distilled to remove volatile components and the yellow residue (2.2 g) was examined by glpc and infrared spectroscopy. A purity greater than 90% was indicated by glpc and absorptions at 6.5, 7.0, and 11.75 μ suggested a triazine structure with only one CF_3 group attached to the ring.

Coupling of Ia.—A quantity of Ia (1.4 g) and Hg (6.6 g) was sealed in a small Carius tube, with the exclusion of air, and heated at 180° for 16 hr and at 250° for 6 hr. The reaction mixture was extracted with methylene chloride and the extract was examined by glpc; a 50% conversion to a higher boiling material was indicated. The higher boiling material (IIa) was

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[14] P. Tarrant, A. Lovelace, and M. Lilyquist, *J. Am. Chem. Soc.*, **77**, 2783 (1955).

[15] W. L. Reilly, Ph.D. Thesis, University of Florida, 1955.

separated from a 25-μl sample of the crude product using preparative gas chromatography (Table III).

Coupling of Ib. Preparation of the Linear Dimer, Trimer, and Tetramer of Ib.—A glass ampoule was charged with 25.2 g of Ib and 330 g of Hg and sealed with exclusion of air. After being heated for 16 hr at 155° the reaction mixture was extracted with hexafluoroxylene and filtered, and the filtrate was examined by glpc; the presence of coupled products was indicated. Pure samples of the three lower boiling coupled products were separated by preparative glpc and identified as IIb dimer, IIb trimer and IIb tetramer (Table III). The infrared spectrum of each compound showed an absorption at 6.48 μ for $C{=}N$.

Coupling of Ib. Preparation of Prepolymer.—A well-stirred mixture of 3590 g of Hg and 549 g of Ib was heated to 175° momentarily and then cooled to 160° where the reaction was allowed to continue for 20 hr under a N_2 atmosphere. The cooled, solid reaction mixture was extracted with CH_2Cl_2 and the extract was separated by filtration. The solvent was removed with a rotary evaporator leaving 373 g of a light tan, waxy solid (Table III). Glpc analysis indicated the presence of approximately 65% dimer and 30% trimer with traces of monomer and higher molecular weight species varying from tetramer to octamer. Bromine analysis indicated an average degree of polymerization of 3–4. An infrared spectrum of a film cast from ether showed 6.45 (s) μ, $C{=}N$.

Coupling of Ib. Preparation of Low Polymer.—A well-stirred mixture of 734 g of Ib and 724 g of Hg was heated at 160° for 6 hr under a N_2 atmosphere. An additional 1448 g of Hg was added in 362-g increments after 6, 23, 32.5 and 54.5 hr. After 60 hr the syrupy reaction mixture was cooled, chipped out of the flask, and ground in a ball mill for several hours. The low polymer was isolated from the mercury and mercury salts in several batches using a variety of extracting solvents: acetone, isopropyl acetate, and ethyl acetate. The total low polymer obtained (410 g) represents an 89.6% yield assuming an average degree of polymerization of 35–40, as indicated by bromine analysis (Table III).

Coupling of Ib. Preparation of High Polymer.—A mixture of 272 g of Hg and 20.7 g of Ib was sealed in a Pyrex ampoule with the exclusion of air and heated at 200° for 16 hr while being rocked. The reaction mass was extracted with boiling hexafluoroxylene for 4 hr and then filtered. The filtrate was freed of solvent to yield 9.1 g of a light tan powder, mp 120–155°. The insoluble portion was digested in cold aqua regia to remove the mercury and mercury salts, leaving 3.1 g of a light tan solid which did not melt below 350° and whose bromine analysis indicated an average (n) of approximately 350 (Table III).

Coupling of IIb (Dimer). Preparation of High Polymer.—A gently stirred mixture of 3.16 g of IIb (dimer) and 1 ml of mercury was gradually heated to 330° for 4 hr under a N_2 atmosphere. After cooling, the clear, amber polymer was peeled off the stirring blade. This polymer did not melt or change appearance at 310° in air for 6 hr.

Coupling of IIb (Low Polymer).—A mixture of 52.6 g of IIb (low polymer) and 50 g of mercury was heated at 300° for 1 hr under a nitrogen atmosphere. The clear, amber polymer (34 g) did not melt below 320° in air.

Attempted Coupling of Ic.—A mixture of 10 g of Hg and 9.1 g of Ic was sealed in a glass ampoule with the exclusion of air and heated at 250° for 16 hr, with rocking. The brown liquid product was examined with glpc and found to contain approximately 96% Ic and 4% IIc.

Attempted Coupling of Id.—A mixture of 0.6 g of Id and 7.35 g of Hg was sealed in a glass ampoule with the exclusion of air and heated at 250° for 19 hr. The colorless liquid product was examined by glpc and found to be pure Id.

Registry No.—Ia, 7601-94-7; Ib, 7601-95-8; Ie, 7648-29-5; CF_2ICO_2Et, 7648-30-8; CF_2ICONH_2, 7601-96-9; CF_2ICN, 7601-97-0; $(CF_2BrCO)_2O$, 7601-98-1; CF_2BrCN, 7601-99-2; Ic, 7602-00-8; Id, 368-66-1; If, 7650-61-5; IIa ($Y = F$; $n = 2$), 7594-83-4; IIb ($Y = Br$; $n = 2$), 7594-80-1; IIb ($Y = Br$; $n = 3$), 7594-81-2; IIb ($Y = Br$; $n = 4$), 7594-82-3.

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Conformation and the Anomeric Effect in 2-Halotetrahydropyrans

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Conformational equilibria of 2-chlorotetrahydropyran, 2-chloro-4-methyltetrahydropyran, 2-bromotetrahydrahydropyran, 2-bromo-4-methyltetrahydropyran, 2-iodotetrahydropyran, and 2-iodo-4-methyltetrahydropyran were examined by nmr methods. The anomeric effects for the chloro and bromo substituents, respectively, were found to be 2.7 and 3.2 kcal/mole or greater. The anomeric effect is rationalized semiquantitatively in terms of the electrostatic interaction of bond dipoles emphasizing the importance of microscopic dielectric constants.

The conformational preference of most substituent groups larger than hydrogen on the cyclohexane ring is for the equatorial position rather than the axial position. However, there are situations where electronegative groups prefer the axial conformation. Such a case exists in the pyranosides where a C-1 methoxyl, acetoxyl, or chloro substituent is more stable in the axial conformation.[1,2] This effect in pyranosides has been called the "anomeric effect."[3] Edward first attributed the anomeric effect to the interaction of the electronegative substituent at the anomeric position with the unshared pairs of electrons of the ring oxygen.[4] Since then the anomeric effect has been more simply attributed to the dipolar interaction of the bond from the pyranoside C-5 to ring oxygen with the bond from the anomeric carbon to the oxysubstituent. The anomeric effect has been explicitly defined as equal to the observed free-energy difference between anomers plus the conformational preference (or A value) for the anomeric substituent, since these effects are opposed at the anomeric position.[5] Other cases of electronegative groups favoring the axial orientation are found in *trans*-2,5-dichloro-1,4-dioxane,[6] *trans*-2,3-dichlorotetra-

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