

added. After cooling during the initial, mild exotherm, the solution was kept overnight at room temperature. After drying *in vacuo*, the clear sirupy residue weighed 26.4 g. (99%). *Anal.* Calcd. for $C_4H_{12}PO_3 \cdot I$, 47.7. Found: I, 47.2. Solution in water and addition of an equivalent of sodium tetraphenylboron gave a white solid of m.p. 170–171° dec. after drying and recrystallization from acetone–benzene. *Anal.* Calcd. for $C_{28}H_{32}PBO_3 \cdot C$, 73.37; H, 7.04; P, 6.76. Found: C, 73.30; H, 6.99; P, 6.27.

n-Butyltris-(hydroxymethyl)-phosphonium Iodide.—An ethanol solution of tris-(hydroxymethyl)-phosphine was prepared from 10.0 g. (0.25 mole) of sodium hydroxide and 47.5 g. (0.25 mole) of THPC under N_2 and treated, after filtration, with 132 g. (0.72 mole) of *n*-butyl iodide. After standing overnight and drying, first with water-pump vacuum and finally at 80–90° with an oil-pump, there was obtained 73.5 g. (95% yield) of clear liquid. *Anal.* Calcd. for $C_7H_{14}PO_3 \cdot I$, 41.2. Found: I, 39.1. Treatment of an aqueous solution with sodium tetraphenyl boron gave a white solid which was washed with water, dried and recrystallized from acetone–benzene; m.p. 145–146° dec. *Anal.* Calcd. for $C_{31}H_{38}PBO_3$: C, 74.40; H, 7.65; P, 6.19. Found: C, 74.18; H, 7.52; P, 6.68.

Hydroxymethylmethyldiphenylphosphonium Iodide.—Sodium (2.3 g., 0.10 g. atom) in 150 ml. of ethanol, after complete reaction was added under N_2 to 28.3 g. (0.10 mole) of bis-(hydroxymethyl)-diphenylphosphonium chloride in 250 ml. of ethanol at 40° in 20

minutes. After 30 minutes, the mixture was filtered to remove sodium chloride and heated at 40–50° in vacuum to give 20.7 g. (96%) of waxy, hygroscopic solid. The solid was dissolved in 75 ml. of ethanol and treated with 30 g. (0.20 mole) of methyl iodide in an ice-bath (exotherm). After 30 minutes, cooling was discontinued and the solution was kept 2 hours at room temperature, then dried in vacuum to give 30.5 g. (85%) of waxy solid, m.p. 223–225° (dec.) after recrystallization from methanol–benzene. *Anal.* Calcd. for $C_{14}H_{11}PO \cdot I$: C, 46.95; H, 4.50; P, 8.65; I, 35.43. Found: C, 47.58; H, 4.83; P, 9.03; I, 34.67.

Hydroxymethyldiisobutylmethylphosphonium Iodide.—Sodium (2.3 g., 0.10 g. atom) was allowed to react with 150 ml. of ethanol and the solution was added to 24.3 g. (0.10 mole) of bis-(hydroxymethyl)-diisobutylphosphonium chloride in 100 ml. of ethanol in 20 minutes under N_2 at ambient temperatures. After standing overnight, sodium chloride was filtered under N_2 pressure and the filtrate was dried to give 17.3 g. (98%) of oily residue. The residue was dissolved in 75 ml. of acetone and treated with 28 g. (0.20 mole) of methyl iodide in an ice-bath. After standing overnight and removal of volatiles, 24.6 g. (77%) of soft solid remained. A portion of this product in water was converted to the tetraphenyl borate which was washed with water and dried; m.p. 168–170°. Recrystallization from acetone–benzene gave m.p. 176–177°. *Anal.* Calcd. for $C_{34}H_{44}PBO$: C, 79.99; H, 8.69; P, 6.07. Found: C, 80.13; H, 8.97; P, 6.26.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

The Action of Elementary Fluorine upon Organic Compounds. XXVI. The Direct Fluorination of Some Perfluoroalkyl-*s*-triazines¹

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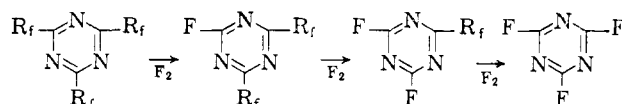
The direct vapor-phase fluorination of tris-(trifluoromethyl)- and tris-(pentafluoroethyl-*s*-triazines has been studied under a variety of operating conditions. When a packed T-reactor was employed, a novel substitution reaction occurred in which the perfluoroalkyl groups were progressively replaced by fluorine yielding some interesting unsymmetrical-*s*-triazines. The new perfluorinated secondary amines $C_2F_5NFC_2F_5$, $CF_3NFC_3F_7$ and $C_2F_7NFC_2F_7$ were also isolated. The jet fluorination of these two triazines led to the formation of several unsaturates including $CF_3CF=NC_2F_5$, $CF_3N=CFC_2F_5$, $C_2F_5CF=NC_3F_7$ and $CF_3CF=NF$ together with their saturated analogs.

Recently the direct fluorination of the simple *s*-triazine cyanuric fluoride⁵ has been found to yield several new highly fluorinated heterocyclic compounds, together with a number of unusual saturated and unsaturated cleavage products. By analogy, it seemed likely that the fluorination of the related compounds tris-(trifluoromethyl)-*s*-triazine, $(CF_3CN)_3$, (I), and tris-(pentafluoroethyl-*s*-triazine, $(C_2F_5CN)_3$, (II), would yield equally interesting results.

The resistance of perfluoroalkyl-*s*-triazines toward fluorination has been demonstrated by Young,⁶ who has reported that only a limited reaction occurred between I and an excess of silver difluoride at 150°. The stability of the triazine nucleus toward free radical attack was more strikingly demonstrated during the present research, since even under the most drastic fluorinating conditions used, considerable amounts of the reactant were recovered. Contrary to the results of the fluorination of cyanuric fluoride, which yielded both tetra- and hexafluoride adducts, II gave no stable ring adduct, although in the case of I there was spectroscopic evidence indicating that an impure product, b.p.

near 93°, may have contained the corresponding tetrafluoride-adduct.

Instead it was found that the perfluoroalkyl groups of I and II were progressively replaced by fluorine as



It is of interest that the infrared spectra of these replacement products exhibited a regular relationship between the degree of substitution and the locations of the planar ring stretching absorptions. As expected, this substitution was favored by vigorous operating conditions especially when a packed T-reactor was employed.

In the case of I, the unsymmetrical-*s*-triazines produced were 2,4-bis-(trifluoromethyl)-6-fluoro-*s*-triazine and 2,4-difluoro-6-trifluoromethyl-*s*-triazine, which were identified spectroscopically. Both of these have been prepared earlier by a different method.⁷ The fluorination of II yielded 2,4-bis-(pentafluoroethyl)-6-fluoro-*s*-triazine and the new 2,4-difluoro-6-pentafluoroethyl-*s*-triazine. The synthesis of the former compound has recently been reported by Kober,⁸ who prepared it by the reaction of 2,4-bis-(pentafluoroethyl)-6-chloro-*s*-triazine with several different fluorinating agents. The structures of both of these perfluoroethyl-*s*-triazines were established by spectroscopic and chemical evidence. The neutral hydrolysis of the former yielded the new pentafluoropropionylurea, indicating ring cleavage,

(7) E. Kober and C. Grundmann, *ibid.*, **81**, 3769 (1959).

(8) E. Kober, H. Schroeder, R. F. W. Rätz, H. Ulrich and C. Grundmann, *J. Org. Chem.*, **27**, 2577 (1962).

(1) This paper has been constructed in part from a portion of the Doctorate thesis submitted by John B. Hynes to the Graduate School of Duke University in June, 1961. Part of this material was presented to the Fluorine Symposium at the Chicago Meeting of the American Chemical Society in September, 1961. This work was supported by the Army Research Office (Durham), the Advanced Research Projects Agency and the Allied Chemical Corporation, to whom grateful acknowledgment is hereby made.

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(4) A.R.O.D. Research Associate, 1961.

(5) J. B. Hynes and L. A. Bigelow, *J. Am. Chem. Soc.*, **84**, 2751 (1962).

(6) J. A. Young, W. S. Durrell and R. D. Dresdner, *ibid.*, **82**, 4553 (1960).

TABLE I
 PHYSICAL PROPERTIES OF LINEAR PRODUCTS

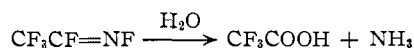
Compound	B.p., °C. (mm.) (extrap.)	ΔH_{vap} , kcal./mole	Trouton's const., cal./deg. mole	Mol. wt.	
				Obsd.	Calcd.
III $\text{CF}_3\text{NFCF}_2\text{CF}_3$	-3.8	6.06	22.5	220	221
IV $\text{CF}_3\text{CF}_2\text{NFCF}_2\text{CF}_3$	23.9	6.58	22.2	268	271
V $\text{CF}_3\text{NFCF}_2\text{CF}_2\text{CF}_3$	24.3	6.37	21.4	270	271
VI $\text{CF}_3\text{CF}_2\text{CF}_2\text{NFCF}_2\text{CF}_2\text{CF}_3$	73 (754)	357	371
VII $\text{CF}_3\text{CF}=\text{NCF}_2\text{CF}_3$	12.8	6.73	23.6	230	233
VIII $\text{CF}_3\text{N}=\text{CFCF}_2\text{CF}_3$	13.2	6.65	22.7	230	233
IX $\text{CF}_3\text{CF}_2\text{CF}=\text{NCF}_2\text{CF}_2\text{CF}_3$	58 (756)	331	333

while that of the latter led to the previously unreported 2,4-dihydroxy-6-pentafluoroethyl-*s*-triazine. It should be noted that similar hydrolytic reactions have been observed for the analogous unsymmetrical trifluoromethyl-*s*-triazines.⁷

In addition to these substitution products, the fluorinations also yielded a number of interesting linear compounds. Only saturated fragments were obtained from the T-reactor, while the jet reactor yielded several corresponding unsaturates as well. The fluorination of I produced perfluoro-2-azabutane, $\text{CF}_3\text{NFC}_2\text{F}_5$ (perfluoromethylethylamine), (III), and perfluoro-3-azapentane, $\text{C}_2\text{F}_5\text{NFC}_2\text{F}_5$ (perfluorodiethylamine), (IV); while that of II gave as expected perfluoro-2-azapentane, $\text{CF}_3\text{NFC}_3\text{F}_7$ (perfluoromethyl-*n*-propylamine), (V), and perfluoro-4-azaheptane, $\text{C}_3\text{F}_7\text{NFC}_3\text{F}_7$ (perfluorodi-*n*-propylamine), (VI). The isolation of III was first reported in an earlier paper from this Laboratory,⁹ but its structure was completely confirmed during the present work. The physical constants of these four new perfluorinated secondary amines are presented in Table I, and the structure of each of them was confirmed by n.m.r. spectroscopy.

In addition to these saturates, the fluorination of I and II in a single jet reactor also yielded several interesting related unsaturates. These were always isolated with their corresponding saturated analogs, from which they could not be separated by fractional distillation. The fluorination of I produced pentafluoro-1-azaprop-1-ene, $\text{CF}_3\text{CF}=\text{NF}$; heptafluoro-2-azabut-2-ene, $\text{CF}_3\text{N}=\text{CFCF}_3$; and nonafluoro-3-azapent-2-ene, $\text{CF}_3\text{CF}=\text{NC}_2\text{F}_5$, (VII); while that of II gave nonafluoro-2-azapent-2-ene, $\text{CF}_3\text{N}=\text{CFC}_2\text{F}_5$ (VIII); and tridecafluoro-4-azahept-3-ene, $\text{C}_2\text{F}_5\text{CF}=\text{NC}_3\text{F}_7$, (IX). The physical properties of the last three are also recorded in Table I.

The mass spectrum of $\text{CF}_3\text{CF}=\text{NF}$ was in accord with its structure since it showed a parent ion, which is characteristic of highly fluorinated unsaturates, and also indicated the presence of C-C and N-F bonding. The infrared spectrum exhibited a band at 5.89 μ , proving that it could not be the other isomer, $\text{CF}_3\text{N}=\text{CF}_2$. A small sample, separated by analytical chromatography, was hydrolyzed to trifluoroacetic acid and ammonia, thus confirming the presence of a C-C bond.

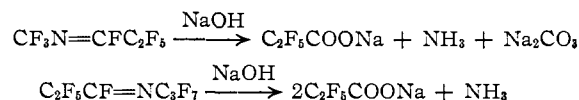


The quantity of pure material available was not sufficient for the measurement of other physical properties. Heptafluoro-2-azabut-2-ene was identified by its known infrared spectrum.

The next higher unsaturated homolog, nonafluoro-3-azapent-2-ene (VII), was separated from its corresponding saturate IV by preparative chromatography. It has previously been reported¹⁰ but no confirming physical data were presented.

The isomer of VII, $\text{CF}_3\text{N}=\text{CFC}_2\text{F}_5$, (VIII), was formed during the fluorination of II in the jet reactor as

well as the higher boiling compound, $\text{C}_2\text{F}_5\text{CF}=\text{NC}_3\text{F}_7$ (IX). After purification by preparative chromatography, both compounds were hydrolyzed by aqueous NaOH to give sodium pentafluoropropionate and ammonia.



The former also yielded carbonate, thus establishing the presence of a $\text{CF}_3\text{N}=\text{C}<$ group. The assigned structures of the three unsaturated compounds VII, VIII and IX were fully confirmed by their F^{19} n.m.r. spectra. It is interesting to note that the infrared spectra of these three unsaturates were very similar in the C=N stretching region, since they exhibited absorptions at 5.58, 5.60 and 5.60 μ , respectively.

The direct fluorination of these perfluoroalkyl-*s*-triazines has led to the formation of several new and interesting compounds resulting from either substitution or cleavage. It is felt that these reactions demonstrate still further the value of the direct fluorination process in the elucidation of the chemistry of unreactive molecules.

Experimental

Apparatus and Materials.—The fluorination reactors, operating techniques and rectification procedures used in this study were essentially the same as those described in the two preceding papers in this series.⁹

The $(\text{CF}_3\text{CN})_3$ and the $(\text{C}_2\text{F}_5\text{CN})_3$ were obtained by the trimerization of the corresponding monomers, CF_3CN and $\text{C}_2\text{F}_5\text{CN}$, which were supplied by Peninsular Chemresearch, Inc. These reactions¹¹ were carried out in stainless steel cylinders, with 0.5 mole of HCl per mole of nitrile as catalyst, at room temperature and under autogenous pressure for 48 hr. Distillation yielded fractions which boiled at 94–96° and 124–126°, respectively. The fluorine, rated as better than 99% pure, was furnished in cylinders by the General Chemical Co., and was used as previously described.

The Separation and Identification of the Products.—The analytical chromatographic separations were carried out with a Barber-Coleman gas chromatograph, model 23-C, using the following packings in 0.25" o.d. copper columns: a, for mixtures b.p. -80 to +40°, Kel-F oil 30%, 15 ft.; b, for mixtures b.p. 40–80°, hexadecane 25%, 12 ft.; c, for mixtures b.p. 80–120°, dioctyl phthalate 30%, 12 ft. Preparative separations were made with a Fisher Prep, partitioner using 0.5- to 1.0-cc. sample injections and the columns; A, Kel-F oil 30%, external copper tube 0.75" o.d. by 16 ft.; B, hexadecane 25%, external copper tube 0.75" o.d. by 16 ft.; C, dioctyl phthalate 25%, 1.0" o.d. glass columns, effective length 14 ft. Chromosorb-P (60–80 mesh) was used in all cases as the solid support.

After preparative separations the purities of all compounds were checked by analytical chromatography, and the final purity in all cases was 99% or better.

All infrared spectra were measured with a Perkin-Elmer model 21 spectrophotometer, while the mass spectra were determined with a Bendix Aviation Corp. Time of Flight Mass Spectrometer.

The Fluorination of $(\text{CF}_3\text{CN})_3$, (I).—This compound has been fluorinated under various operating conditions in both the jet and packed T-reactors. In all, 8 runs were made and the detailed results of a representative jet fluorination are given in Table II. Results obtained from the T-reactor were much the same, except that only saturated fragments were formed and somewhat better yields of the unsymmetrically substituted *s*-triazines were obtained.

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

(10) W. H. Pearson and L. J. Hals, U. S. Patent 2,643,267 (1953).

(11) E. R. Bissell and R. E. Speuger, *J. Org. Chem.*, **24**, 1147 (1959).

TABLE II

THE RECTIFICATION OF FLUORINATED (CF₂CN)₃

Sample used 47.2 g.; flow rate, 0.020 mole/hr.; molar ratio (F₂:(CF₂CN)₃:N₂), 8:1:60; temp., 240°; crude yield, 37 cc.

Fraction	Boiling range, °C. (mm.)	Mol. wt.	Yield of crude prod. (%)	Principal components
1	-129 to -126	83-87	35	CF ₄ + NF ₃
2	-79 to -78	132-135	8	C ₂ F ₆
3	-75 to -40	125-150	1.5	Transition
4	-39.5 to -35	167-175	7	CF ₃ CF ₂ NF ₂ + (CF ₃) ₂ NF
5	-35 to -15	175-180	1.5	Contains CF ₃ CF=NF
6	-14.5 to -10.5	188-190	5	CF ₂ N=CFCF ₃ + CF ₂ NFC ₂ F ₅
7	-5 to -3	217-220	4	CF ₂ NFC ₂ F ₅ + CF ₂ N=NC ₂ F ₅
8	-8 to -4 (364)	220-230	2.5	Transition
9	-4 to -3 (364)	234-239	2.5	CF ₂ CF=NC ₂ F ₅ + (C ₂ F ₅) ₂ NF
10	0 to 20 (364)	250-310	5
11	Residue	27

The well-known low boiling products which were always formed were identified and discarded. The higher boiling mixtures could not be resolved by rectification, but were separated and purified by chromatography.

Pentafluoro-1-azaprop-1-ene, CF₃CF=NF.—Fraction 5 contained, along with the known C₂F₅NF₂, a small amount of an unsaturate which could not be separated by preparative chromatography. It was finally isolated in pure condition (0.1 cc.) by repetitive analytical chromatography over Florisil at room temperature. The infrared spectrum showed that it contained a C=N bond (absorption at 5.89 μ), and that it was not its isomer CF₃N=CF₂.¹² The mass spectrum exhibited the following *m/e* values in order of decreasing intensity: 69(CF₃⁺), 31(CF⁺), 114(C₂F₄N⁺), 50(CF₂⁺), 133(C₂F₅N⁺) (parent ion), 45(CFN⁺), 26(CN⁺), 64(CF₂N⁺), 95(C₂F₃N⁺), 12(C⁺), 100(C₂F₄⁺), 76(C₂F₂N⁺), 19(F⁺), 33(FN⁺), 38(C₂N⁺) and 119(C₂F₅⁺), the pattern being consistent with the proposed structure. On hydrolysis with water in a sealed tube for 24 hr. at room temperature, it yielded NH₃ and CF₃COOH, the latter being identified by its infrared spectrum.

Perfluoro-2-azabutane, CF₃NFC₂F₅ (III), and Heptafluoro-2-azabut-2-ene, CF₃N=CFCF₃.—Fraction 6 was found to contain CF₂NFC₂F₅ and also its corresponding known unsaturate CF₂N=CFCF₃, and could not be resolved by distillation. The former, previously reported from this Laboratory,⁹ was obtained in pure condition by bubbling the mixture through 10% aqueous NaOH which destroyed the unsaturate. Its F¹⁹ n.m.r. spectrum, which was incorrectly reported earlier,⁹ exhibited four peaks, the corrected values referred to CF₃COOH being -6.96 p.p.m. (CF₂ on N), +7.85 p.p.m. (CF₂ on CF₂), +13.89 p.p.m. (NF) and +36.0 p.p.m. (CF₂). The relative areas were also in accord with the assigned structure.

The unsaturate CF₂N=CFCF₃, which was separated by analytical chromatography, was identified by its infrared spectrum.¹² It exhibited an absorption at 5.57 μ, which was clearly different from the C=N stretching bands reported for its isomers (CF₂)₂C=NF¹² (6.05 μ) and C₂F₅N=CF₂¹³ (5.52 μ).

Perfluoro-3-azapentane, C₂F₅NFC₂F₅ (IV), and Nonfluoro-3-azapent-2-ene, CF₂CF=NC₂F₅ (VII).—Fraction 9 was shown to contain the new (C₂F₅)₂NF, and its corresponding known unsaturate CF₂CF=NC₂F₅.¹⁰ When the latter was removed by destructive hydrolysis, the pure saturate was obtained. A considerable quantity of this material was isolated by combining similar fractions from several runs, and eventually purified by distillation; b.p. (extrapolated) 23.9°, mol. wt. 268 (calcd. 271). The infrared spectrum showed no unsaturation and was otherwise consistent with the assigned structure. The mass spectrum exhibited the following *m/e* values in order of decreasing intensity: 119(C₂F₅⁺), 69(CF₃⁺), 31(CF⁺), 202(C₂F₅N⁺), 50(CF₂⁺), 114(C₂F₄N⁺), 100(C₂F₄⁺), 252(C₄F₁₀N⁺), 52(C₂N₂⁺), 164(C₃F₈N⁺), 76(C₂F₂N⁺), 95(C₂F₄N⁺), 64(CF₂N⁺), 152(C₂F₅N⁺), 271(C₄F₁₁N⁺) (parent ion), 45(CFN⁺), 33(FN⁺), 81(C₂F₃⁺) and 83(CF₂N⁺). The F¹⁹ n.m.r. spectrum showed absorptions at +7.02 p.p.m. (CF₃), +16.4 p.p.m. (NF) and +32.8 p.p.m. (CF₂), referred to CF₃COOH, whose relative areas were in accord with the assigned structure.

The corresponding unsaturate VII was finally separated by preparative chromatography using packing A, b.p. 12.8° (extrapolated), mol. wt. 230 (calcd. 233). The infrared spectrum exhibited a band at 5.58 (C=N), and the F¹⁹ n.m.r. spectrum showed four absorptions at -46.9 p.p.m. (CF), -1.4 p.p.m. (CF₂ next to CF), +10.6 p.p.m. (CF₂ next to CF₂) and +22.0 p.p.m. (CF₂), relative to CF₃COOH consistent with the structure.

2,4-Difluoro-6-trifluoromethyl-s-triazine(i) and 2,4-Bis-(trifluoromethyl)-6-fluoro-s-triazine(ii).—The high boiling residue from the



fluorination (fractions 10 and 11) was analyzed by chromatography using a 6-ft. Kel-F column at room temp. and it was found to contain 2,4-difluoro-6-trifluoromethyl-s-triazine, 8%; 2,4-bis-(trifluoromethyl)-6-fluoro-s-triazine, 30%, unreacted starting material, 55% and traces of (FCN)₃. The percentages were estimated from relative peak areas. Their infrared spectra showed the characteristic absorptions due to the s-triazine system. The mass spectra of these two triazines were examined and both spectra were relatively simple. 2,4-Difluoro-6-trifluoromethyl-s-triazine exhibited the following *m/e* values in order of decreasing intensity: 69(CF₃⁺), 31(CF⁺), 185(C₄F₅N₃⁺) (parent ion), 71(C₂F₂N₂⁺) 90(C₂F₂N₂⁺), 45(CFN⁺), 50(CF₂⁺), 166(C₄F₄N₃⁺), 116(C₂F₂N₃⁺), 76(C₂F₂N⁺), 140(C₂F₄N₂⁺), 52(C₂N₂⁺), 57(C₂FN⁺), 114(C₂F₄N⁺), 59(CFN₂⁺), 97(C₂FN₃⁺) and 159(C₃F₅N₂⁺); while 2,4-bis-(trifluoromethyl)-6-fluoro-s-triazine showed: 69(CF₃⁺), 71(C₂FN₂⁺), 31(CF⁺), 235(C₅F₇N₄⁺) (parent ion) 117(C₂F₃⁺), 119(C₄F₄N⁺), 140(C₃F₄N₂⁺), 216(C₅F₈N₃⁺), 76(C₂F₂N⁺), 50(CF₂⁺), 121(C₃F₃N₂⁺), 43(C₂F⁺), 45(CFN⁺) and 166(C₄F₄N₃⁺). These two triazines have previously been prepared by a different route.⁷

The Fluorination of (C₂F₅CN)₃(II).—This compound has also been fluorinated under various operating conditions in both the jet and packed T-reactors. In all, 12 runs were made, and the detailed results of a representative jet fluorination are given in Table III.

TABLE III

THE RECTIFICATION OF FLUORINATED (C₂F₅CN)₃

Sample used, 87.5 g.; flow rate, 0.020 mole/hr.; molar ratio (F₂:(C₂F₅CN)₃:N₂), 8:1:55; temp., 190°; crude yield, 50 cc.

Fraction	Boiling range, °C.	Mol. wt.	Yield of crude prod. (%)	Principal components
1	-120 to -118	82-85	7	CF ₄
2	-94 to -80	86-136	7	Transition
3	-75	138	30	C ₂ F ₆
4	-41 to -30	155-191	18	C ₂ F ₅ + (CF ₃) ₂ NF
5	-3 to -6	200-230	8	C ₂ F ₇ NF ₂ + CF ₂ N=CFC ₂ F ₅
6	Residue		7	CF ₂ NFC ₂ F ₅ + CF ₂ N=CFC ₂ F ₅

Then the high boiling portion (13 cc.) was distilled in a 12'' fractionating column, yielding fraction 7, b.p. 58-80° 3.7 cc. (C₂F₇)₂NF + C₂F₅CF=NC₂F₇ and residue, 10 cc. (C₂F₅CN)₃ 70% + other triazines.

Perfluoro-2-azapentane, CF₂NFC₂F₅ (V), and Nonfluoro-2-azapent-2-ene, CF₂N=CFC₂F₅ (VIII).—From an experiment in the T-reactor, one fraction was found to contain a large amount of CF₂NFC₂F₅, which was purified by preparative chromatography with column A. It boiled at 24.3° (extrapolated) and its mol. wt. was 270 (calcd. 271). Its infrared spectrum was consistent and its F¹⁹ n.m.r. spectrum showed absorptions at -7.7 p.p.m. (CF₃ on NF), +6.1 p.p.m. (CF₂ on CF₂), +12.4 p.p.m. (NF), +33.2 p.p.m. (CF₂ next to NF) and +51.0 p.p.m. (CF₂ next to CF₂), referred to CF₃COOH. The relative peak areas were in accord with the assigned structure.

Later it was shown that fraction 6 (above) contained mostly CF₂NFC₂F₅ accompanied by its corresponding unsaturate CF₂N=CFC₂F₅, which was purified by preparative chromatography using column A. It boiled at 13.2 (extrapolated), mol. wt. 230 (calcd. 233). The infrared spectrum exhibited a band at 5.60 μ (internal C=N). The F¹⁹ n.m.r. spectrum showed absorptions at -51.2 p.p.m. (CF on N), -18.3 p.p.m. (CF₃ on N), +7.3 p.p.m. (CF₃ on CF₂), +44.6 p.p.m. (CF₂), referred to CF₃COOH. The relative areas were in the ratio of 0.96:2.96:2.98:2.07 consistent with the structure. On hydrolysis with 10% NaOH in a sealed tube for 24 hr. at room temperature, it yielded carbonate, NH₃ and C₂F₅COONa, which was identified by its infrared spectrum.

Perfluoro-4-azaheptane, (C₂F₇)₂NF (VI), and Tridecafluoro-4-azahept-3-ene, C₂F₇CF=NC₂F₇ (IX).—Fraction 7 was subjected to preparative chromatography with column B at room temperature yielding (C₂F₇)₂NF and C₂F₇CF=NC₂F₇. The former boiled at 73° (754 mm.) with mol. wt. 357 (calcd. 371). Its infrared spectrum showed no unsaturation, and was otherwise consistent. The F¹⁹ n.m.r. showed four absorptions at +5.75 p.p.m. (CF₂), +13.8 p.p.m. (NF), +29.2 p.p.m. (CF₂ next to NF) and +50.0 p.p.m. (CF₂ next to CF₂), referred to CF₃COOH, with relative areas of 6.5:1:4.1:4.1 consistent with the structure.

The corresponding unsaturate IX boiled at 58.5° (756 mm.), mol. wt. 331 (calcd. 333). The infrared spectrum exhibited an absorption at 5.60 μ (internal C=N). Its F¹⁹ n.m.r. spectrum

(12) R. D. Dresdner, private communication.

(13) D. A. Barr, R. N. Haszeldine and C. J. Willis, *J. Chem. Soc.*, 1351 (1961).

showed six absorptions at: -53.1 p.p.m. (CF), $+5.58$ p.p.m. (CF₂), $+7.60$ p.p.m. (CF₃), $+18.3$ p.p.m. (CF₂ next to N), $+45.2$ p.p.m. (CF₂) and $+53.3$ p.p.m. (CF₂), referred to CF₃COOH, with the relative areas of 1.0:3.2:3.2:2.0:1.9:2.1 in agreement with the assigned structure. On hydrolysis with 10% NaOH in a sealed tube for 24 hr. at room temperature, it yielded C₂F₅COONa and NH₃, as expected.

2,4-Difluoro-6-pentafluoroethyl-*s*-triazine (iii) and 2,4-Bis-(pentafluoroethyl)-6-fluoro-*s*-triazine (iv).—The high boiling



residues from the fluorinations of (C₂F₅CN)₃ in the packed T-reactor were combined and fractionated using a 12'' column packed with glass helices to give three fractions: (a) b.p. 90–98° (3 cc.), (b) 98–115° (4 cc.) and (c) residue of unreacted (C₂F₅CN)₃. Fraction a was subjected to preparative chromatography with column C at 80°, and yielded 2,4-difluoro-6-pentafluoroethyl-*s*-triazine, b.p. 94.5° at 753 mm. The infrared spectrum showed the characteristic absorptions of an *s*-triazine system. On hydrolysis with excess cold water for 0.5 hr., it yielded 2,4-dihydroxy-6-pentafluoroethyl-*s*-triazine monohydrate, m.p. 167–168°, which was not dehydrated over P₂O₅ at 100° for 4 hr. Its infrared spectrum was similar to those of other dihydroxy-*s*-triazines, and an absorption at 5.85 μ indicated that the molecule existed partially in the ketonic form.

Anal. Calcd. for C₈H₂F₈N₃O₂·H₂O: C, 24.1; H, 1.6; F, 38.2. Found: C, 24.3; H, 1.7; F, 37.9.

Then fraction b was subjected to preparative chromatography with column C at 80° and yielded 2,4-bis-(pentafluoroethyl)-6-fluoro-*s*-triazine, b.p. 112° at 753 mm. (known,⁸ 106° at 760

mm.). Its infrared spectrum also exhibited absorptions characteristic of an *s*-triazine system. The mass cracking pattern exhibited the following *m/e* values in order of decreasing intensity: 69(CF₃⁺), 76(C₂F₂N⁺), 71(C₂FN₂⁺), 121(C₃F₃N₂⁺), 119-(C₂F₃⁺), 266(C₄F₂N₃⁺), 50(CF₂⁺), 100(C₂F₄⁺), 102(C₃F₂N₂⁺), 57(C₂FN⁺), 126(C₃F₄N⁺), 176(C₄F₆N⁺), 14(N⁺), 45(CFN⁺), 26(CN⁺), 38(C₂N⁺), 52(C₂N₂⁺), 107(C₃F₃N⁺), 316(C₇F₁₀N₃⁺), 335(C₇F₁₁N₃⁺) (parent ion), 216(C₅F₈N₃⁺), 40(CN₂⁺), and 197-(C₅F₆N₃⁺), in accordance with the assigned structure. The F¹⁹ n.m.r. spectrum of 2,4-bis-(pentafluoroethyl)-6-fluoro-*s*-triazine showed absorptions at -42.0 p.p.m. (C-F), $+9.6$ p.p.m. (CF₃) and $+46.4$ p.p.m. (CF₂), referred to CF₃COOH, the relative areas of which were approximately 1:6:4 consistent with the structure. The hydrolysis of this triazine was more difficult than that of the preceding one, but after warming the mixture for 1 hr. it yielded pentafluoropropionylurea, m.p. 194–196°.

Anal. Calcd. for C₄H₃F₈N₃O₂: C, 23.3; H, 1.5; F, 46.2. Found: C, 23.1; H, 1.7; F, 46.1.

This compound was independently synthesized by the reaction of pentafluoropropionic anhydride and urea, and was identical to the hydrolysis product by mixed melting point. The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

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The Equilibration of Cyclic Allenes and Acetylenes¹

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Allene-acetylene equilibria have been established for the C₉, C₁₀- and C₁₁-cyclic systems in *t*-butyl alcohol employing potassium *t*-butoxide as a catalyst. From the temperature dependence of the equilibrium constants the enthalpies of isomerization for the change acetylene → allene, have been found to be (in kcal./mole): C₉, -2.56 ; C₁₀, -0.45 ; and C₁₁, $+1.35$. These results show that ring-strain is more pronounced in cyclic acetylenes than in cyclic allenes. The solvent effects and a method for evaluating them are discussed.

In this paper we examine the relative thermodynamic stabilities of certain cyclic acetylenes and allenes. Although acetylene-allene interconversions have been known for many years and numerous examples have appeared (reviewed in ref. 3–6), most of the observations have not been of value in establishing relative thermodynamic stabilities.

From published thermodynamic data^{7–11} it is possible to devise the diagram shown as Fig. 1 which interrelates

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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(11) (a) Standard heats of formation at 25° in the gas phase were taken from the following references: ref. 7, acetylene, 1-propyne, allene; ref. 8, 1- and 2-pentyne (see below); ref. 9, 1- and 2-butyne, 1,2- and 1,3-butadiene; ref. 10, 1,2-, 1,3-, 1,4- and 2,3-pentadiene. (b) The heat of formation of 2-pentyne is given as 30.80 ± 0.50 kcal./mole in ref. 8 (which refers to unpublished data). Examination of the changes in the heats of formation within

the energies of isomeric acyclic acetylenes and dienes. The values given for enthalpies (heats) of isomerization should be accurate to within a few tenths of a kilocalorie. These data indicate that a terminal allene is of slightly lower energy than an isomeric terminal acetylene, but that an internal acetylene should be significantly lower in energy than an isomeric internal (1,3-disubstituted) allene. All allenes and acetylenes possess much higher energies than isomeric unconjugated dienes which, as is well-known, have higher energies than the conjugated dienes.¹²

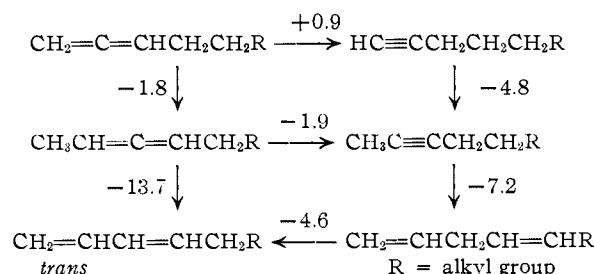


Fig. 1.—Approximate standard enthalpies in kcal./mole of isomerization of gaseous acetylenes and dienes at 25°.

various homologous series (ref. 7) as well as reference to the other data indicated above strongly suggest that this value is too high. We have used the value of 29.9 kcal./mole which appears to be internally consistent.

(12) The discussion here is in terms of enthalpies; the free energy changes should at least parallel the enthalpy changes.