Further since

$$x = \exp(\Delta E_{I}/RT)$$
$$y = \exp(\Delta E_{II}/RT)$$

the relation $x = y$ is indicated. This derivation ignores second-order effects such as bond deformation would introduce, and must be regarded as approximate only. Also the calculation of $J_{1,4}{}^{I}$ and $J_{1,4}{}^{II}$ from eq. 2 and 3 with $x = y$ is made with the implicit assumption that J_g and J_t are constant in a series of hydrocarbons and this may introduce further error.

Nevertheless, on this basis it is predicted that since $x = 1$ for butene, $y = 1$ for 3-methylbutene, and this compound should also be characterized by a $J_{1,4}$ essentially equal to that of propene. Such is indeed the case.

In the case of the mono- and di-*tert*-butyl derivatives, it is possible to estimate J_g, J_t, and x, all from the experimental data using eq. 1, 2, and 3, together with the additional relation $x = y$.

The relations obtained by solving eq. 1, 2, and 3 for x and J_g are

$$x = 2(J_{1,4}{}^{1} - J_{1.4}{}^{II})/(3J_{1,4}{}^{0} - 4J_{1.4}{}^{I} + J_{1,4}{}^{II})$$
$$J_g = (2J_{1,4}{}^{0}J_{1,4}{}^{II} - J_{1,4}{}^{I}(J_{1,4}{}^{0} + J_{1.4}{}^{II}))/(J_{1.4}{}^{0} + J_{1,4}{}^{II} - 2J_{1,4}{}^{I}) \quad (6)$$

The value for J_t may then be found by substituting in the relation

$$J_t = 3J_{1,4}{}^{0} - 2J_g$$

For the *tert*-butyl series, the value of x obtained by substitution in these relations is quite sensitive to the observed values of $J_{1,4}{}^{0}$, $J_{1,4}{}^{I}$ and $J_{1.4}{}^{II}$ used, varying from 10 to ∞ with changes in the second decimal place of these values. The derived values of J_g and J_t are quite constant, however. Using the approximate values 6.3, 7.5 and 10.7 for $J_{1,4}{}^{0}$ $J_{1,4}{}^{I}$ and $J_{1,4}{}^{II}$, respectively, one obtains the results $x = 16$, $J_g = 3.7$, $J_t = 11.6$. These values reinforce earlier conclusions concerning J_g and J_t. The value of x obtained implies that the mono-*tert*-butyl compound is largely in forms I_a and I_b, and the di-*tert*-butyl compound is predominantly in form II_a.

Finally, $J_{1,4}$ in the compound 1,1-dimethyl-3,3-di-*tert*-butylpropene-1 has the value 11.37 c.p.s., which must very nearly represent J_t. Models indicate a very high energy for conformers of this molecule with *tert*-butyl and isopropylidene groups eclipsed.

The data also confirm in a very satisfactory manner the suggestion of Whipple, Goldstein and McClure[9] that the allylic couplings $J_{2,4}$ and $J_{3,4}$ vary with rotational conformer population and are smallest in magnitude in the conformer with eclipsed methylene and allylic proton. The effect of conformer population on these coupling constants (as well as on $J_{1,4}$) is most strikingly displayed in the data obtained for 3,3-di-*tert*-butylpropene-1 (Table I).

Di-*tert*-butylacetaldehyde was prepared in the course of the synthesis of di-*tert*-butylpropylene, and, in view of the findings of Abraham and Pople,[12] it also appeared of interest to investigate the coupling constants in this case. The coupling constant between the aldehyde proton and the proton on the adjacent carbon had the value 5.0 c.p.s.; *i.e.*, considerably larger than acetaldehyde (2.8 c.p.s.). This suggests that steric interference between the *tert*-butyl group and the carbonyl when they are eclipsed is large, so that the conformer with the carbonyl and proton eclipsed (analogous to II_a) is favored. The explanation for the preferred conformation of propionaldehyde (analogous to I_c), is probably the same as that advanced by Szasz[28] for the preferred *gauche* conformation of *n*-propyl chloride.

Acknowledgments.—Mrs. O. D. Geisel developed the program for the IBM 704 high speed computer whereby least-squares fitting of observed spectra was performed. Dr. E. Hackel prepared a number of the compounds which were studied. This work was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under contract No. AF 49(638)980.

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[28] G. J. Szasz, *J. Chem. Phys.*, **23**, 2449 (1955).

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

The Action of Elementary Fluorine Upon Organic Compounds. XXV. The Direct Fluorination of Cyanuric Fluoride[1]

BY JOHN B. HYNES[2] AND LUCIUS A. BIGELOW

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Cyanuric fluoride has been fluorinated in both the jet and T-reactors under a variety of operating conditions. There were formed in considerable yields heptafluoro-1,3,5-triazacyclohexene (tetrafluoride adduct), perfluoro-1,3,5-triazacyclohexane (perfluoro-*s*-triazine) and perfluoro-1,3-diazacyclopentane (perfluoroimidazolidine), the last involving a ring contraction. Fragmentation also occurred with the formation in small amounts of the linear products $CF_3NFCF_2NFCF_2NF_2$, $CF_3NFCF_2NFCF_3$ and several others whose structures have been assigned on the basis of spectroscopic evidence. The physical properties of these new compounds have been presented, and a mechanistic interpretation of this reaction has been proposed.

Cyanuric fluoride, $(FCN)_3$, which may be regarded either as the acid fluoride of cyanuric acid or as the cyclic trimer of cyanogen fluoride, was reported first from this laboratory by Maxwell.[3]

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[1] This paper has been constructed from portions of the Doctorate thesis submitted by John B. Hynes to the Graduate School of Duke University in June, 1961. Most of this material was presented to the Fluorine Symposium at the Chicago, Ill., Meeting of the American Chemical Society in September, 1961.

[2] Allied Chemical Corporation Fellow 1960–1961 and Army Research Office (Durham) Research Associate 1961–1962. Grateful Acknowledgment is hereby made for this generous support.

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

It is a colorless liquid, boiling at 74°, which is very sensitive to hydrolysis but otherwise quite stable. It has recently been shown by Young[4] that this triazine system on treatment with silver difluoride under pressure at 150° yielded only small amounts of known fragments, over half of the reactant being recovered. Thus it was considered that the direct fluorination of this relatively simple, pseudo-aromatic system should be of interest since it might be expected to lead to the formation of new highly fluorinated heterocyclic compounds by the direct addition of fluorine to the ring.

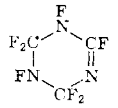
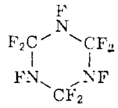
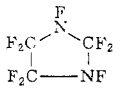
Accordingly, the direct fluorination of cyanuric fluoride (I) has been studied under a variety of operating conditions in both a modified single jet reactor and also in the older packed T-reactor. Each yielded essentially the same principal products, but the former favored the production of unsaturated materials, while the latter gave the highest yield of the desired perfluoro-1,3,5-triazacyclohexane (perfluoro-*s*-triazine). It should be noted here that for the sake of consistency in the nomenclature of highly fluorinated organic compounds containing nitrogen the well-known syllable aza will be used to denote the replacement of carbon by nitrogen in either the aliphatic or alicyclic series. Thus, for example, the compound $CF_3NFCF_2NFCF_3$ would be named perfluoro-2,4-diazapentane.

Under mild operating conditions in the jet reactor the fluorination of I produced, among other substances, the tetrafluoride adduct heptafluoro-1,3,5-triazacyclohexene (II) which was a pale yellow liquid, b.p. 56°, obtained in 20% yield. Under all operating conditions, and especially in the T-reactor, Compound I was easily converted into the fully saturated perfluoro-1,3,5-triazacyclohexane (III) which was a colorless stable liquid, b.p. 51°, obtained in a maximum yield of 38%. At the same time another new and very interesting cyclic product was nearly always formed, apparently by rearrangement involving a ring contraction. The compound, which was assigned the structure perfluoro-1,3-diazacyclopentane (IV) was a colorless liquid, b.p. 29°, obtained in a maximum yield of 40%. These yields were based on the total volume of the product minus the volume of I recovered, and in most cases were estimated chromatographically. The physical properties of these new cyclic products are shown in Table I, all samples being better than 99% pure by analytical chromatography.

The unique unsaturate II, like other compounds containing the C=N linkage, was sensitive to hydrolysis and attacked glass rapidly. When it was heated under pressure with anhydrous hydrogen fluoride the expected adduct was formed in small yield. It had a retention time on di-*n*-octyl phthalate approximately twice that of II, and showed infrared absorptions at 2.87 and 6.64 μ. The absorptions at 2.89 and 6.65 μ of the related compound CF_3NHCF_3 have been assigned by Barr[5] to the N–H stretching and bending vibrations, respectively.

TABLE I

PHYSICAL PROPERTIES OF NEW COMPOUNDS

Compound	Structure	B.p., °C. (extrap.) F.p., °C.	ΔH vap.	Trouton's constant	Mol. wt. Obsd. Calcd.
II		56 −104	6.8	20.7	215 211
III		51 − 79	6.9	21.3	247 249
IV		29 −105	7.18	23.7	218 216
VI	$CF_3NFCF_2NFCF_3$	23 ..	6.65	22.4	.. 254

The fully saturated product III was as expected highly stable chemically, and its structure was confirmed by its molecular weight and n.m.r. spectrum.

Perhaps the most interesting aspect of this fluorination was the formation of perfluoro-1,3-diazacyclopentane (IV). By way of analogy, it should be noted that a similar ring contraction occurred in the fluorination of benzene, in which one of the principal products was perfluorocyclopentane, as reported from this Laboratory by Fukuhara.[6] The new compound IV was obtained very pure and was fully saturated according to its infrared spectrum. However, it attacked glass slowly at room temperature and was partially hydrolyzed when passed through cold 10% aqueous base yielding ammonia, carbonate, fluoride and oxalate. Also when pyrolyzed over steel gauze at 435°, it yielded only CF_4, C_2F_6 and a trace of CHF_3. These results clearly indicate the presence of a C–C bond in the molecule, and strongly suggest the assigned structure, which was further corroborated by mass spectral data. At first sight it might be considered that such a saturated cyclic structure should not be sensitive to hydrolysis. However, this instability may well be accounted for by strain due to the distortion of C–N–C bond angles in the formation of the five-membered heterocyclic ring. It should also be noted that the analogous imidazolidines are readily hydrolyzed by cold dilute mineral acids.

These cyclic compounds were always accompanied by a number of linear cleavage products in varying amounts depending upon operating conditions. Of these, the well-known ones always present were CF_4, NF_3, CF_3NF_2, $(CF_3)_2NF$, $CF_3N=NCF_3$ and under the more vigorous operating conditions $(CF_3)_3N$. Interestingly enough these same materials were also produced by the fluorination of cyanogen, hydrogen cyanide, methylamine and ethylenediamine as previously reported[7] from this Laboratory. Small quantities of three other saturated linear compounds were isolated chroma-

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[4] J. A. Young, W. S. Durrell and R. D. Dresdner, *J. Am. Chem. Soc.*, **82**, 4553 (1960).

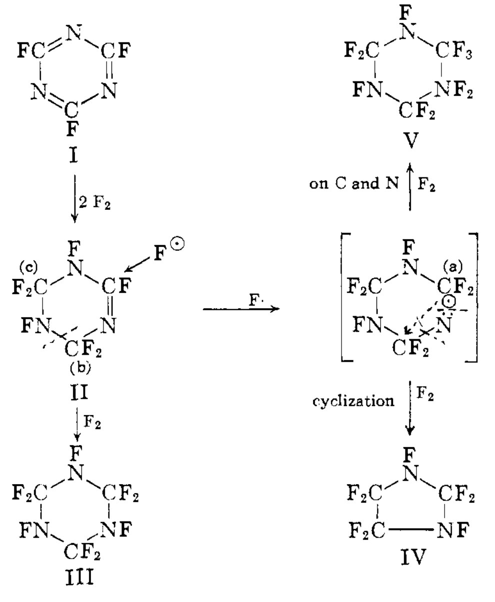
[5] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 4169 (1955).

[6] N. Fukuhara and L. A. Bigelow, *J. Am. Chem. Soc.*, **63**, 2792 (1941).

[7] P. R. Robson, V. C. R. McLoughlin, J. B. Hynes and L. A. Bigelow, *ibid.*, **83**, 5010 (1961).

tographically from the more vigorous fluorinations. Based upon their infrared spectra, mass cracking patterns and relative retention times, they were believed to possess the interesting structures $CF_3NFCF_2NFCF_2NF_2$ (V), $CF_3NFCF_2NFCF_3$ (VI) and $CF_3NFCF_2NF_2$ (VII), all of which may be regarded as reasonable products of the progressive degradation and saturation of I by fluorine. The structures of V and VI have been further confirmed by n.m.r. spectroscopy. In addition, the jet reactor yielded small quantities of two other isomeric unsaturated products, which have been tentatively assigned the structures $CF_3NFCF{=}NCF_3$ (VIII) and $(CF_3)_2NCF{=}NF$ (IX) on the basis of spectroscopic evidence. The former is a reasonable fragmentation product of I, and the latter may well have been obtained from its isomer by rearrangement. It is also of interest that in all of the fragmentation products V–IX the carbon and nitrogen atoms are alternately placed as they are in I.

So far as a mechanism is concerned, the direct addition of fluorine to I to form II and III requires no special comment. However, in the case of the ring contraction, it is assumed that this occurs before the ring is fully fluorinated, since III is almost certainly resistant to further attack under the conditions involved. If the attack of a high energy fluorine atom at the unsaturated carbon of II causes the dissociation of the double bond, perhaps through a nitrene, followed by cyclization and the expulsion of nitrogen eventually as an $\cdot NF_2$ radical, then the formation of IV may readily be accounted for as indicated in the accompanying scheme. It is noteworthy that traces of N_2F_4 were formed in several of the fluorinations.



Alternatively, if carbon atom (a) in the intermediate accepted another fluorine and the adjacent nitrogen was also fully fluorinated, this would easily account for the formation of the longest linear fragment V. The latter, in turn, could be readily degraded into VI and VII by repeated attack of fluorine on saturated carbons with the expulsion of nitrogen leading to the formation of NF_3. On the other hand, if II were attacked at saturated carbon (b), opening the ring as indicated by the dotted line, followed by further attack at (c) resulting in the cission of the terminal C–N bond, this would lead to the production of VIII with the double bond still intact. This linear unsaturate could also be converted into VI and thence into VII. The isomerization of VIII into IX as well as the formation of $CF_3N{=}NCF_3$ and $(CF_3)_3N$ can be accounted for by mechanisms analogous to those presented in the previous paper of this series.[7]

The preparation of the tetra- and hexafluoro adducts of cyanuric fluoride in substantial quantities demonstrates the value of controlled elementary fluorination techniques since less potent reagents have been ineffective toward this end. Furthermore, this indicates that the direct fluorination of other pseudo-aromatic systems containing nitrogen should be of considerable interest.

Experimental

Apparatus.—Unless otherwise noted the fluorinations were carried out in a single jet two-stage reactor, the final modification of which has been described by Maxwell.[8] However, the $^1/_{16}''$ brass jet was replaced by a similar one of stainless steel in order to reduce the gradual deterioration of the orifice. On account of the easy hydrolysis and toxic nature of cyanuric fluoride, the sample was introduced on nitrogen from a specially designed glass flask saturator, capacity 80 cc., which was equipped with standard taper joints and appropriate stopcocks. The carrier gas was admitted through a vertical tube provided with a sintered glass disk at the lower end, while the exit tube to the side was connected by a Tygon sleeve to a 3-way stopcock through which a secondary nitrogen stream was admitted not only to dilute the sample further, but also to resist any possible back pressure of fluorine. The main line was then connected directly to the reactor jet.

In operation the secondary nitrogen stream was first started and fluorine then passed through the heated reactor for approximately 0.5 hour. Then metered nitrogen was bubbled through the sample at room temperature and the stopcock simultaneously adjusted so that the two gas streams were mingled and passed directly into the jet. The average molar flow rate, which was determined by weighing the saturator before and after the reaction, could be controlled by varying either the flow rate of the carrier gas or the temperature of the saturator, or both. After this had been determined the molar fluorination and dilution ratios could be controlled by adjusting the fluorine and secondary nitrogen flow rates accordingly. The products were collected in refrigerated glass traps as usual, and other details of the manipulation were conventional.

Chromatographic separations were made using a Perkin–Elmer model 154 vapor fractometer or a Fisher prep.-partitioner. The packings used were essentially the same as those reported earlier.[7] The 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.

Materials.—The cyanuric fluoride, which was prepared by the method of Maxwell,[8] boiled at 74° and was chromatographically pure. The fluorine, rated as better than 99% pure, was supplied in cylinders by the General Chemical Co., and was measured by a calibrated rotameter. Commercial nitrogen, OP grade, was supplied by the Air Reduction Co.

The Fluorination of Cyanuric Fluoride.—The sample was fluorinated using the apparatus and operating techniques just described. In all eight significant runs were made, and the results are shown in Table II. In all cases the known relatively low boiling products always formed in varying amounts were merely identified and then discarded. They were NF_3, CF_4, CF_3NF_2, $(CF_3)_2NF$ and $CF_3N{=}NCF_3$.

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(8) A. F. Maxwell, F. E. Detoro and L. A. Bigelow, *J. Am. Chem. Soc.*, **82**, 5827 (1960).

TABLE II

THE FLUORINATION OF CYANURIC FLUORIDE

Run	Oper. time, hr.	Flow rate moles/hr.	Molar ratio $F_2:(FCN)_3:N_2$	Temp., °C. Stages 1	Temp., °C. Stages 2	Liq. vol. % of total product B.p. > −30°	Liq. vol. % of total product $(FCN)_3$ recovd.	G. $(FCN)_3$ recovd./ G. $(FCN)_3$ used
1	2.5	0.025	7:1:40	165	170	11	5	0.09[b]
2	3.5	.029	3:1:35	166	175	39	9	.10
3	3.5	.027	3:1:37	135	135	41	18	.22
4	7.0	.027	3:1:37	120	119	50	11	.15
5	5.0	.036	2.3:1:28	100	102	73	23	.25
6	6.0	.027	3:1:37	78	78	86	28	.44
7[a]	6.0	.039	2.3:1:51	83	..	81	24	.41
8	12.0	.040	2.5:1:20.6	88	92	81	15	.20

[a] Operated in a packed T-reactor. [b] The density of $(FCN)_3$ used in this calculation was experimentally determined to be 1.60 ± 0.05 g./cc., and the amount of sample used was weighed.

Accordingly, the table shows only the operating conditions used and the proportions of the total product in each case boiling above −30°, which contained all of the new and significant compounds formed in the reaction. The amounts of unchanged cyanuric fluoride recovered were estimated by direct measurement, since the reactant was immiscible with the fluorinated products below 0°, and then checked by chromatographic peak areas.

Clearly the greatest amount of the desired material was obtained at the lower temperatures. Experience soon showed, however, that this material could not be separated into pure components by rectification even under the best conditions. Therefore, the crude fractions were separated into pure components by preparative vapor phase chromatography and the new compounds identified by their physical and spectroscopic properties, as described in the following sections.

Heptafluoro-1,3,5-triazacyclohexene, $C_3F_7N_3$ (II) was purified by vapor phase chromatography (v.p.c.) over 20% hexadecane-on-Chromosorb P using a 16 ft. × 0.75″ o.d. copper tube column. It had b.p. 56° (extrapolated), f.p. −104°, mol. wt. 215 (calcd. 211) and was obtained in 20% yield from run 6. The ΔH vap. and Trouton's constant were calculated to be 6.8 kcal./mole and 20.7 cal./deg. mole, respectively. The infrared spectrum showed a band at 5.73 μ, indicating C═N unsaturation. The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 128($C_2F_4N_2^+$), 69(CF_3^+), 83(CF_3N^+), 31(CF^+), 50(CF_2^+), 109($C_2F_3N_2^+$), 95($C_2F_3N^+$), 114($C_2F_4N^+$), 64(CF_2N^+), 45(CFN^+), 71($C_2FN_2^+$), 192($C_3F_6N_3^+$), 90($C_2F_2N_2^+$), 166($C_2F_6N_2^+$), 147($C_2F_5N_2^+$), 59(CFN_2^+), 33(FN^+), 76($C_2F_2N^+$), 12(C^+), 159($C_3F_5N_2^+$), 173($C_3F_5N_3^+$), 211($C_3F_7N_3^+$) parent ion, 78($CF_2N_2^+$), 47.5($C_2F_3N^{++}$), 135($C_3F_3N_3^+$), 19(F^+), 26(CN^+), 40(CN_2^+) and 38(C_2N^+), the pattern being entirely consistent with the proposed structure. The n.m.r. spectrum was inconclusive, presumably because the sample reacted with glass. This compound was a yellow liquid, sensitive to hydrolysis, which did not appear under the more vigorous operating conditions. It had a chromatographic retention time on hexadecane which was intermediate between that of I and III.

The hydrogen fluoride adduct to this unsaturate was prepared by heating about 1 g. (0.6 cc.) of the compound with an excess of HF in a 10-cc. stainless steel cylinder for 10 hr. at 100°. The sample was condensed into the cylinder, and the HF drawn in from a 1-cc. syringe. The product was passed over KF, condensed in a glass trap, and analyzed by v.p.c., showing the presence of two high boiling compounds, one of which was identical to II. The infrared spectrum of the mixture showed not only the peaks due to II, but also absorptions at 2.87 and 6.64 μ, characteristic of the N–H stretching and bending vibrations in highly fluorinated nitrogen compounds.

Perfluoro-1,3,5-triazacyclohexane, $(CF_2NF)_3$ (III) was purified by v.p.c. using hexadecane-on-Chromosorb W. It had b.p. 51° (extrapd.), f.p. −79° (sharp), mol. wt. 247 (calcd. 249) and was obtained in 38% yield from run 7. In all cases the yields are expressed as volume per cent of the crude product excluding unreacted I, as estimated by relative chromatographic peak areas. The ΔH vap. and Trouton's constant were calculated to be 6.9 kcal./mole and 21.3 cal./deg. mole, respectively. The infrared spectrum showed no unsaturation, and a strong band at 10.52 μ, indicating N–F bonding. The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 83(CF_3N^+), 69(CF_3^+), 166($C_2F_6N_2^+$), 114($C_2F_4N^+$), 147($C_2F_5N_2^+$), 50 (CF_2^+), 31(CF^+), 64(CF_2N^+), 128($C_2F_4N_2^+$), 45(CFN^+), 95($C_2F_3N^+$), 59(CFN_2^+), 33(FN^+), 71($C_2FN_2^+$), 90($C_2F_2N_2^+$), 12(C^+), 109($C_2F_3N_2^+$), 230($C_3F_8N_3^+$) and 249($C_3F_9N_3^+$) parent ion. This pattern is similar to that for perfluorocyclohexane, since the parent ions of both molecules constitute a very small percentage of the total ionization. The n.m.r. spectrum showed only two peaks, one at +11.8 p.p.m. (N–F), and the other at +12.8 p.p.m. (CF_2) relative to CF_3COOH. The relative peak areas were as 1.77 to 3.57; ratio 1:2.02 (calcd. 1:2.0).

Perfluoro-1,3-diazacyclopentane, $C_3F_8N_2$ (IV) was purified by v.p.c. (better than 99%) using both hexadecane and Kel-F columns. It had b.p. 29° (extrap.), f.p. −105° (sharp), mol. wt. 218 (calcd. 216) and was obtained in 40% yield from run 8. The ΔH vap. and Trouton's constant were calculated to be 7.18 kcal./mole and 23.7 cal./deg. mole, respectively. The infrared spectrum showed no unsaturation, and an absorption at 10.62 μ, indicating N–F bonding. The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 50(CF_2^+), 69(CF_3^+), 128($C_2F_4N_2^+$), 109($C_2F_3N_2^+$), 31(CF^+), 114($C_2F_4N^+$), 78($CF_2N_2^+$), 64(CF_2N^+), 83(CF_3N^+), 45(CFN^+) 95($C_2F_3N^+$), 152($C_2F_6N^+$), 102(CF_4N^+), 33(FN^+), 166($C_2F_6N_2^+$), 147($C_2F_5N_2^+$), 90($C_2F_2N_2^+$), 76($C_2F_2N^+$), 100($C_2F_4^+$) and 185($C_2F_7N_2^+$). This pattern showed no parent ion, but did have a peak at mass 100($C_2F_4^+$), indicating C–C bonding in the compound.

When this compound was bubbled slowly through 10% aqueous NaOH, about 50% of it reacted, and when the basic solution was heated it evolved ammonia (basic gas). When a portion of the liquid was neutralized with dilute HCl it effervesced vigorously and CO_2 was liberated as detected by the $Ca(OH)_2$ test. Then the solution was boiled for 15 min. until no more volatile acid (HF + HCl) was evolved (NH_3 test), after which it was cooled and a few drops of $Ca(NO_3)_2$ solution added. No precipitation occurred at first, but when an equal volume of ethanol was added, a fine white precipitate separated, which was presumed to be calcium oxalate.

The five aliphatic fragments obtained have been examined in the following manner.

Perfluoro-1,3,5-triazahexane, $CF_3NFCF_2NFCF_2NF_2$ (V).—A small quantity of this material was obtained from run 7. Its retention time on hexadecane was slightly less than that of III, indicating that it boiled just below 50°, while its infrared spectrum was in accord with the assigned structure. The mass spectrum exhibited the following *m/e* values in order of decreasing intensity: 69(CF_3^+), 152($C_2F_6N^+$), 102(CF_4N^+), 185($C_2F_7N_2^+$), 83(CF_3N^+), 50(CF_2^+), 114($C_2F_4N^+$), 31(CF^+), 64(CF_2N^+), 52(NF_2^+) and 33(NF^+). As expected, the n.m.r. spectrum exhibited 6 peaks whose chemical shifts relative to CF_3COOH and assignments were: −95.2 p.p.m. (NF_2), −7.4 p.p.m. (CF_3), +7.9 and +8.9 (N–F), +15.0 (CF_2 between 2NF's), and +25.6 (CF_2 next to NF_2). The relative areas were in complete accord with the assigned structure.

Perfluoro-2,4-diazapentane, $CF_3NFCF_2NFCF_3$ (VI) was purified by V.P.C. using a 6-ft. Kel–F analytical column. Its extrapolated boiling point was 23° while its ΔH vap. and Trouton's constant were 6.65 kcal./mole and 22.4 cal./deg. mole, respectively. It was obtained in approximately 3% yield from run 7. The infrared spectrum showed no unsaturation, a band at 10.21 μ indicating N–F bonding, and was generally similar to that of $(CF_3)_2NF$ in the 8 to 11 μ region. The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 69(CF_3^+), 152 ($C_2F_6N^+$), 59(CFN_2^+), 50(CF_2^+), 31(CF^+), 114($C_2F_4N^+$), 83(CF_3N^+), 64(CF_2N^+) and 133 ($C_2F_5N^+$). The n.m.r. spectrum showed only three peaks at −7.2 (CF_3), at +8.7 (N–F), and at +17.3 ppm. (CF_2), all relative to CF_3COOH. The respective peak areas were also in accord with the proposed structure. The new saturate was colorless and occurred mixed with the corresponding unsaturated VIII in varying proportions. The unsaturate in the mixture could readily be destroyed by hydrolysis, leaving the saturate essentially pure.

Perfluoro-1,3-diazabutane, $CF_3NFCF_2NF_2$ (VII).—A small quantity of this compound was isolated by v.p.c. on Florisil from the more vigorous fluorinations. Its retention time was slightly less than that of its isomer $NF_2CF_2CF_2NF_2$, b.p. −1.6°, indicating that its boiling point was slightly below −2°. The infrared spectrum was complex in the N–F region, showing a strong band at 10.53 μ and a weaker one at 10.82 μ. The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 69(CF_3^+), 50(CF_2^+), 102(CF_4N^+), 152($C_2F_6N^+$), 31(CF^+), 83(CF_3N^+), 33(FN^+), 64(CF_2N^+), 52(F_2N^+), 12(C^+), 45(CFN^+), 114($C_2F_4N^+$), 97($CF_3N_2^+$), 19(F^+), 147($C_2F_5N_2^+$), 166($C_2F_6N_2^+$), 40(CN_2^+), 95($C_2F_3N^+$), 76($C_2F_2N^+$), 128($C_2F_4N_2^+$), 133($C_2F_5N^+$) and 185 ($C_2F_7N_2^+$). The relative abundance of the peaks at mass 33(NF) and 52(NF_2) strongly suggested the presence of more than one type of N–F bonding in this molecule, as did the infrared spectrum.

Octafluoro-2,4-diazapent-2-ene, $CF_3NFCF{=}NCF_3$ (VIII) was separated in small amounts by v.p.c. from complex mixtures boiling in the 0° to 20° range, and was obtained from the milder fluorinations. Its b.p. as estimated from its retention time was between 15° and 20°. The infrared spectrum showed a strong band at 5.62 μ, indicating internal C=N bonding. The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 69(CF_3^+), 114($C_2F_4N^+$), 109($C_2F_3N_2^+$), 31(CF^+), 50(CF_2^+), 152($C_2F_6N^+$), 197($C_3F_7N_2^+$), 64(CF_2N^+), 45(CFN_2^+), 216($C_3F_8N_2^+$) parent ion, 128($C_2F_4N_2^+$), 83(CF_3N^+), 12(C^+), 147($C_2F_5N_2^+$), 95($C_2F_3N^+$) 47(FN_2^+), 71($C_2FN_2^+$), 90($C_2F_2N_2^+$), 19(F^+), 59(CFN_2^+), 26(CN^+) and 33(FN^+).

This colorless compound was readily hydrolyzed by water at room temperature. The resulting solution contained no CF_3COOH, but evolved NH_3 on treatment with base. This indicated the absence of terminal C–C bonding, and the presence of a C=N group, thus supporting the proposed structure.

Octafluoro-3-methyl-1,3-diazabut-1-ene, $(CF_3)_2NCF{=}NF$ (IX).—This pure isomer of VIII was separated by v.p.c. from the same complex mixture as above, but had a somewhat shorter retention time indicating a b.p. near 10°. The infrared spectrum showed bands at 5.94 μ (C=N) and 10.56 μ (N–F), as well as at 10.07 μ $(CF_3)_2N$; the last value being well supported by Dresdner.[9] The mass spectrum showed the following *m/e* values in the order of decreasing intensity: 69(CF_3^+), 31(CF^+), 59(CFN_2^+), 50(CF_2^+), 45(CFN^+), 128($C_2F_4N_2^+$), 64(CF_2N^+), 166($C_2F_6N_2^+$), 114($C_2F_4N^+$), 33(FN^+), 12(C^+), 147($C_2F_5N_2^+$), 83(CF_3N^+), 95($C_2F_3N^+$), 26(CN^+), 71($C_2FN_2^+$), 19(F^+), 197($C_3F_7N_2^+$), 47.5($C_2F_3N^{++}$), 135(CF_5N_2), 90($C_2F_2N_2^+$), 109($C_2F_3N_2^+$) and 216($C_3F_8N_2^+$) parent ion. The absence of ions at 119($C_2F_5^+$), 100($C_2F_4^+$) and 81($C_2F_3^+$) indicated clearly that there was no C–C bonding in the molecule, and therefore that the carbon and nitrogen atoms were alternately placed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, AND THE CHEMISCHES LABORATORIUM DER UNIVERSITAT, FREIBURG I. BREISGAU, GERMANY]

Pyridinium Complexes. IV. The Effect of N-Substituents on the Position of the Iodide Charge-transfer Band

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The positions of the iodide charge-transfer bands for a series of substituted 1-X-benzyl-4-carbomethoxypyridinium ions in *cis*-1,2-dichloroethylene are shown to be correlated by the equation $E_T/2.303RT = \rho_s\sigma$, in which σ is the Hammett constant and ρ_s is a sensitivity parameter comparable to the usual ρ. In the present case, $\rho_s = -1.70$, consistent with the large effect of substitution expected for a charge-transfer band. It is suggested that an intramolecular charge-transfer band (i.c.t.) is observed as a shoulder at 3090 Å. in solutions of 1-(4-methoxybenzyl)-4-carbomethoxypyridinium ion (as the perchlorate).

Previous studies of alkylpyridinium iodide charge-transfer bands have indicated that the transition energies are very sensitive to the nature of the substitution on the pyridinium ring.[2,3] We now report data for a series of 1-X-benzyl-4-carbomethoxypyridinium iodides in which it is clear that the charge-transfer band position is very sensitive to even small changes in the electron affinity of the pyridinium ring. A potentially useful correlation with the Hammett σ-constant is also found for the band positions.

Results

Five 1-(X-benzyl)-4-carbomethoxypyridinium iodides (X = 4-NO_2, 4-Cl, H, 4-OCH_3 and 2,6-Cl_2) were prepared. Their charge-transfer bands were measured in the low-polarity solvent, *cis*-1,2-dichloroethylene (**Z**, 63.4).[4] This solvent has the requisite amount of solvent power for alkylpyridinium iodides combined with low ion pair-dissociating power,[4] thus ensuring adequate quantities of ion-pairs even at low solute concentrations. The absorption maxima for the pyridinium iodides are summarized in Table I. Ultraviolet data for the pyridinium perchlorates are given in Table II.

Discussion

The charge redistribution corresponding to the charge-transfer transition of the benzylpyridinium

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