-CF_2- doublet at +100.5 ppm coupled by 22.8 cps to the -NF- at +48.4 ppm are very reasonable for the F_2NCF_2NF- portion of the molecule and in good agreement for the same assignments made for F_2NCF_2NFCN.

The highest boiling product obtained from the fluorination, N[(difluoroamino)difluoromethyl]-N,N′,N′,N″,N″-1-hexafluoromethanetriamine, $(F_2N)_2CFNFCF_2NF_2$, is an explosive, colorless liquid boiling at 60°, extrapolated from vapor pressure–temperature measurements. The molecular weight found by gas density measurements was 267 (calcd 270).

The infrared absorption spectrum in the gas phase showed strong intensity bands in the CF region at 7.85, 8.10, and 8.32 μ. The 7.85-μ band had a shoulder at 7.65 μ. Strong bands at 10.45 and 10.95 μ, usually attributed to NF bonds, and weak bands at 9.45, 9.70, 9.95, 11.50, 11.75, 12.60, and 13.20 μ were also observed. The mass spectrum of $(F_2N)_2CFNFCF_2NF_2$ showed no parent peak. A peak observed at m/e of 218 was assigned to $C_2N_3F_8^+$ which results from loss of NF_2 from the parent molecule. Other major peaks observed which can be accounted for by the structure were at m/e of 147, 128, 135, 116, 102, 83, 69, and 64. The ^{19}F nmr spectrum ($CFCl_3$ as reference) showed five lines consistent with the structure as follows (peak, assignment, relation area): −23.5 ppm, $C(NF_2)_2$, 4; −19.2 ppm, CNF_2, 2; +90.0 ppm, -NF–, 1; +100.4 ppm, -CF_2–, 2; and 131.2 ppm, CF, 1.

Experimental Section

Caution! The products and various unidentified by-products from the fluorination of sodium dicyanamide and cyanoguanidine are extremely explosive in the gas, liquid, and solid state. They have been manipulated routinely in a mercury-free vacuum line with CF_2Cl_2 slush baths at −130 to −145°. It was standard practice to use adequate shielding and protective equipment and to keep the sample size below 0.5 g.

Fluorination of Cyanoguanidine.—Cyanoguanidine (5 g, 60 mmol) was mixed with 50 g of sodium fluoride which had been dried at 110°. The mixture was charged into a three-necked, 1-l. monel flask fitted with a stirrer and gas inlet and outlet. The flask was immersed in an ice bath and stirred while 20–40% fluorine diluted with nitrogen was introduced into the flask at a total gas flow rate of 200–400 ml/min for 60 min. The crude product was collected from the effluent stream in a glass U-trap cooled in a Dry Ice bath. When approximately 0.5 ml of crude product was collected in the U-trap, the trap was removed and additional product was collected in a second and third trap, etc.

Purification of the products was achieved by repeated codistillation[4] using a 10-mm copper column packed with fluorine-treated 40–60 mesh magnesium beads.

Fluorination of $NaN(CN)_2$.—Sodium dicyanamide (2 g, 20 mmol) and 20 g of magnesium fluoride were put into a 500-ml flask fitted with a stirrer, a fluorine inlet, and a gas outlet connected to a Dry Ice cooled trap. The rapidly stirred mixture was cooled in an ice bath and a 50:50 mixture of F_2–N_2 was passed through the flask at 200 cc/min for 60 min. During this time, about 1 cc of liquid was collected in the Dry Ice trap. The product was purified by codistillation.

The infrared data were obtained with a Perkin-Elmer Model 137B spectrophotometer. The cell had a 2.5-cm path length and NaCl windows. The vapor pressure was measured in a mercury-free system from −80 to −2°. The nuclear magnetic resonance spectrum was obtained on an instrument described by Baker and Burd.[5]

Registry No.—Sodium dicyanamide, 4615-74-1; cyanoguanidine, 461-58-5; $(F_2N)_2CFNFCF_2NF_2$, 16408-92-7; $F_2NC({=}NF)NFCF_2NF_2$, 16408-93-8; I, 16408-94-9.

Acknowledgment.—This work was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Air Force Rocket Propulsion Laboratory, under Contact Nr. AF 33-(616)-6149.

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[4] G. H. Cady and D. P. Siegworth, *Anal. Chem.*, **31**, 618 (1959).

[5] E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **34**, 238 (1963); **28**, 313 (1957).

Effect of Fluorine on Photoelimination Reactions in Ketones

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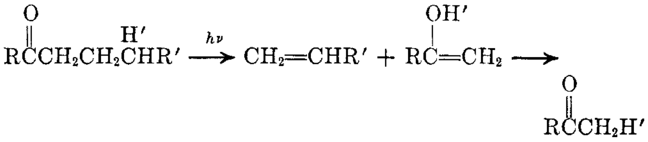
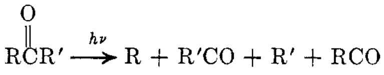
Considerable interest has been shown recently in the type II photolytic process in ketones. Wagner and Hammond[1] and Dougherty[2] have shown that both excited singlet and triplet species can be involved in solution while the work of Coulson and Yang[3] and Wagner[4] indicates that biradical species may also play a role. Earlier, it had been shown by Srinivasan,[5] by means of deuterium substitution, that the γ hydrogen is transferred to the carbonyl oxygen. The over-all process may be represented as



$$\mathrm{R\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{H'}{C}HR' \xrightarrow{h\nu} CH_2{=}CHR' + R\overset{OH'}{\overset{|}{C}}{=}CH_2 \longrightarrow R\overset{O}{\overset{\|}{C}}CH_2H'}$$

Nicol and Calvert[6] have carried out an extensive study of the effect of alkyl substitution on the vapor phase photolysis of a series of n-propyl ketones. Under these conditions the type I process is also important. Essentially no work has been carried out on the effect of substituents other than alkyl at the γ-carbon atom. For this reason we examined the effect of fluorine on the photolysis of 4,6,8,8,8-pentafluoro-3-octanone, $CF_3CH_2CHFCH_2CHFC({=}O)CH_2CH_3$.



$$\mathrm{R\overset{O}{\overset{\|}{C}}R' \xrightarrow{h\nu} R + R'CO + R' + RCO}$$

When irradiated either neat or in hydrocarbon solvents (0.2 M) four products could be detected by glpc. Only two of these could be separated in sufficient amount and purity for identification. 1-Fluoro-2-butanone was identified by comparison with a sample prepared independently from fluoroacetonitrile (Experimental Section). Glpc retention times, infrared, and H^1 and F^{19} nmr spectra were identical. 1,1,1,3,5-Pentafluoropentane was identified by comparison with a sample prepared from the 2:1 telomer of vinyl fluoride and trifluoromethyl iodide (Experimental Section).

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[1] P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

[2] T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

[3] D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

[4] P. J. Wagner, *Tetrahedron Lett.*, **18**, 1753 (1967).

[5] R. Srinivasan, *J. Amer. Chem. Soc.*, **81**, 5061 (1959).

[6] C. H. Nicol and J. G. Calvert, *ibid.*, **89**, 1790 (1967).

Chromatographic and spectral characteristics were identical for the samples. A third material, trapped as a gas from the chromatograph and analyzed by infrared spectroscopy, showed it to contain a fluoro-substituted double bond (1690 cm^{-1}) and a trifluoromethyl group (1280 cm^{-1}). Vinyl-type fluorine was also detected in the photolyzed solution of the fluoro ketone by F^{19} nmr spectroscopy. This compound is tentatively identified as 1,1,1,3-tetrafluoro-3-butene. Its rate of formation by glpc is identical with that of 1-fluoro-2-butanone. The fourth product which could not be separated completely from the starting ketone exhibited a strong OH absorption in the infrared spectrum at 3200 cm^{-1}. This material could be a cyclobutanol derivative, compounds which are often found in low yields in these reactions or a reduction product of the starting material. Yields as measured by glpc are 1-fluoro-2-butanone, 1,1,1,3-tetrafluoro-3-butene, 32%; 1,1,1,3,5,-pentafluoropentane, 16%; alcohol, 21.4%. The material balance leaves 31.6% unaccounted for. That hydrogen fluoride is produced during photolysis is evident by the slow etching of the quartz photolysis cells. It is not known if this derives from starting material or products or both.

The quantum yield at 2537 Å for disappearance of fluoro ketone in heptane solution was determined to be 0.39 by comparison with 2-hexanone which is reported to have a quantum yield of 0.327 at 3130 Å in pentane.[3] An indication of the amount of singlet and triplet reaction involved in the type II process producing 1-fluoro-2-butanone and 1,1,1,3-tetrafluoro-3-butene was obtained by carrying out quenching experiments with piperylene and *cis*-dichloroethylene.[1,2] In each case only 93% of the reaction to form type II products could be quenched, indicating this fraction of triplet reaction. Both pieces of quantitative data are subject to the uncertainties of less than total material balance. This amount of triplet reaction, however, may be compared with 60% for 2-hexanone and 2-octanone under similar conditions. The larger fraction of triplet reaction may be due to the increased energy required for abstraction, by the excited carbonyl group, of a γ hydrogen at a position of low electron density thus allowing for intersystem crossing from excited singlet to excited triplet to compete more effectively. Formation of the type I product, 1,1,1,3,5-pentafluoropentane, in 16% yield is unusual in solution photolyses. In unsubstituted ketones, *e.g.*, 2-hexanone this product generally accounts for less than 3% of the total.[7] (In vapor phase photolysis, on the other hand, type I products generally run well over 50% of the total.) The increased tendency for type I reactions may simply reflect the slower rate of type II reactions with which they compete. However, some increased stability of the intermediate fluoro-substituted radical is also to be expected, *i.e.*

$$CF_3CH_2CHFCH_2\dot{C}HF \longleftrightarrow CF_2CH_2CHFCH_2CH{=}F\cdot$$

Experimental Section

Synthesis of 4,6,8,8,8-Pentafluoro-3-octanone.—3,5,7,7,7-Pentafluoro-2-heptene available from a previous study[8] was oxidized in a typical experiment as follows. To a slurry of olefin (5.0 g, 0.024 mol) in 100 ml of water was added dropwise a solution of potassium permanganate (17 g) and sodium hydroxide (2.0 g) in water (400 ml). After stirring overnight, sodium bisulfite and dilute sulfuric acid were added alternately until the solution became clear. The mixture was then extracted with three 100-ml portions of ether which were dried ($MgSO_4$) and evaporated to yield a white solid (3.8 g, 75%). Separation into two isomers, mp 88–91 and 68–71°, could be achieved by fractional crystallization from a chloroform–petroleum ether (bp 30–50°) solution. Each gave the same average analysis (samples from several runs) and neutral equivalent.

Anal. Calcd for $C_6H_7F_5O_2$: C, 34.9; H, 3.4; F, 46.1; neut equiv, 206. Found: C, 35.3; H, 3.5; F, 45.8; neut equiv, 210.

The mixture of diastereoisomeric acids was converted into the acid chlorides, bp 73–79° (22 mm), in 70% yield by thionyl chloride. The ketone was prepared typically as follows. Diethylcadmium was prepared from ethylmagnesium bromide [from 3.56 g (0.149 g-atom) of Mg, 17.6 g (0.161 mol) of ethyl bromide, and 125 ml of dry ether] and cadmium chloride (13.4 g, 0.073 mol) at ice-bath temperature. After refluxing about 1 hr the slurry was cooled in an ice–salt bath to about −10° and the acid chlorides (20 g, 0.096 mol) in ether (15 ml) were added dropwise over 30 min. The reaction mixture was stirred overnight and cooled and 10% sulfuric acid added slowly until clear. The ether layer was washed with dilute sodium carbonate solution and dried. Evaporation of the ether yielded 14.6 g (92%) of crude product. The oily residue was distilled under reduced pressure, 29–34° (0.05 mm), and purified as follows. The distilled mixture was solidified by cooling in Dry Ice and then partially melted by slowly warming to room temperature. When about one-half of the material had melted, the slurry was rapidly filtered under suction and the solid sucked dry with a rubber dam. The material which remained solid at room temperature was further purified by a combination of recrystallization (ethanol–water) and sublimation, mp 40–41°. The mother liquor could be recycled several times to obtain more solid material. Separation into a liquid and solid form could also be carried out by preparative gas chromatography. These materials had identical infrared spectra (carbonyl at 1730 cm^{-1}) with the exception of the intensity of a peak at 943 cm^{-1}. The fluorine nmr spectrum (60 Mc) showed CF_3 as a complex multiplet at 65.0 ppm (relative to CCl_3F), relative area = 3; –CHF– as a broad unresolved peak centered at 186.3 ppm, relative area = 1; and –C(=O)CHF– as a septet at 193 ppm, relative area = 1. The proton nmr spectrum indicated CH_3 as a triplet (J = 7 cps) at τ 8.96, relative area = 3; the $-CH_2$ group of the ethyl group as a quartet (J = 7 cps) centered at τ 7.46 on top of the remaining methylene groups which occur as a broad unresolved peak centered at approximately τ 7.5, total relative area = 6; and –CHF– as two broad, unresolved doublets (J = 53.4 cps) at τ 5.1, relative area = 2. The ultraviolet spectrum of the solid isomer showed a maximum at 2825 Å (ϵ 26.9) and formed a 2,4-dinitrophenylhydrazone, mp 85–87.5°. Elemental analyses tended to be erratic even with a single sample.

Synthesis of 1-Fluoro-2-butanone.—Fluoroacetamide (Peninsular ChemResearch) was converted in 65% yield into fluoroacetonitrile by reaction with phosphorous pentoxide.[9] To a cold (−15°) ethereal solution of ethylmagnesium bromide prepared from 9.8 g (0.42 g-atom) of magnesium, 45.8 g (0.42 mol) of ethyl bromide, and 125 ml of ether, was added dropwise a solution of fluoroacetonitrile (24.8 g, 0.42 mol) in ether (125 ml). The mixture was stirred overnight and cooled and 10% sulfuric acid slowly added. The ether layer was dried and evaporated to yield a dark oil which was distilled at atmospheric pressure resulting in extensive decomposition. A fraction boiling at 60–120° was purified by gas chromatography. The proton nmr spectrum showed the ethyl group and a fluoromethylene group in 1:1 ratio. The fluorine nmr spectrum indicated a single CH_2F type of fluorine at 228.5 ppm (relative to CCl_3F). The ketone formed a 2,4-dinitrophenylhydrazone, mp 89–90.5°.

Anal. (2,4-DNPh). Calcd for $C_{10}H_{11}N_4O_4F$: C, 44.5; H, 4.07; N, 20.8. Found: C, 43.5; H, 4.3; N, 20.7.

Preparation of 1,1,1,3,5-Pentafluoropentane.—1,1,1,3,5-Pentafluoroamyl iodide[10] (55.7 g, 0.193 mol) dissolved in ethanol (100 ml) was added over 6 hr to a mixture of zinc (38.6 g, 0.59 g-atom) in absolute ethanol (900 ml) saturated with hydrogen

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(7) P. Ausloos and R. E. Rebbert, *J. Amer. Chem Soc.*, **83**, 4897 (1961).

(8) T. J. Dougherty, *ibid.*, **86**, 460 (1964).

(9) R. E. Kent and S. M. McElvain, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 493.

(10) T. J. Dougherty, *J. Amer. Chem. Soc.*, **86**, 2236 (1964).

chloride at 70–80°. Hydrogen chloride was added periodically to maintain saturation. After standing overnight, the mixture was filtered and mixed with water (3000 ml) containing $NaHCO_3$ and extracted with four 100-ml portions of ether. The ether solution was separated, dried ($MgSO_4$), and distilled. After removal of ether and a low-boiling (54–103°) fraction, the pentafluoropentane was collected at 103–105° to yield 6.3 g (19%). The infrared spectrum showed the CH stretch at 2960 cm^{-1} and C-F at 1265 and 1170 cm^{-1}. Unsaturation was absent. The proton nmr spectrum showed the $-CH_2-$ groups as a complex multiplet centered at τ 5.4, relative area = 4; -CHF- as two quintets (J = 6.0 cps) separated by 50 cps, relative area = 1; and $-CH_2F$ at τ 4.5 as two triplets (J = 5.8 cps) separated by 48 cps, relative area = 2.

Anal. Calcd for $C_5F_5H_7$: C, 37.1; F, 58.6; H, 4.3. Found: C, 37.3; F, 58.6; H, 4.4.

Photolysis Procedure.—Photolysis cells of approximately 1.8-ml capacity (1.5 cm long) were filled with a 0.2 M solution of the ketone in heptane (spectroquality), immersed in a quartz circulating water bath at 35 ± 0.5° and exposed to either a low-pressure mercury lamp (>90% uv output at 2537 Å) or a medium-pressure mercury lamp (25% uv output at 3100–3300 Å, 75% at 3300–3700 Å). Degassing (freeze–thaw technique) had no effect on quantum yields. Distilled quencher was added directly from a microliter syringe. Samples of 1 or 2 μl were taken every 20–60 min, depending on the lamp employed, over a period of several hours and analyzed by gas chromatography on a Carbowax 1500 column operated at 140° with a helium flow of 50 cc/min. Runs were carried to approximately 5–25% completion in the case of the quenching experiments utilizing the medium-pressure lamp and up to 75% completion when the 2537-Å lamp was used.

Four photolysis products were detected at retention times of 1.0, 2.2, 3.0, and 15.5 min. The first of these products was gaseous and was collected from the chromatograph in an evacuated infrared gas cell. The infrared spectrum bore a strong resemblance to that of 2,3,5,7,7,7-hexafluoro-1-heptene[10] exhibiting a =CF absorption at 1690 cm^{-1} and a CF_3 absorption at 1280 cm^{-1}. Insufficient material was obtained for further examination. The second eluted product had a retention time and ir spectrum identical with those of 1,1,1,3,5-pentafluoropentane obtained by reduction of the corresponding iodide (see above). The product eluted at 3.0 min proved to be 1-fluoro-2-butanone by comparison with the sample prepared as described above. These materials agreed in retention times as well as infrared and nmr spectra (H^1 and F^{19}). The last eluted product was obtained in only trace amounts and highly contaminated with the starting ketone. However, the presence of a hydroxyl group was apparent in the infrared spectrum at 3200 cm^{-1}.

Registry No.—4,6,8,8,8-Pentafluoro-3-octanone, 16408-87-0; 4,6,8,8,8-pentafluoro-3-octanone 2,4-dinitrophenylhydrazone, 16408-88-1; 1-fluoro-2-butanone, 453-10-1; 1-fluoro-2-butanone 2,4-dinitrophenylhydrazone, 580-05-2; 1,1,1,3,5-pentafluoropentane, 16408-89-2; fluorine, 7782-41-4.

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The Oxidation of Aldehydes in Alcoholic Media with the Caro Acid

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The Caro acid (peroxymonosulfuric acid) has often been used as a characteristic oxidizing agent in the field of organic synthesis. It was early observed that the Baeyer–Villiger reaction occurred in the oxidation of carbonyl compounds with this oxidant as follows.[1]

$$R{-}CO{-}R' + H_2SO_5 \longrightarrow R{-}O{-}CO{-}R' + H_2O + H_2SO_4$$

Oxidation of acrolein in alcoholic media with hydrogen peroxide in the presence of selenium dioxide as catalyst was reported to give acrylates in 15–40% yield.[2] This method was investigated further in oxidation of other aldehydes in methanol or ethanol.[3] Methyl methacrylate was obtained also by the oxidation of methacrolein in methanol with t-butyl hydroperoxide in the presence of metal salt catalysts, such as $FeCl_2$ and $FeCl_3$.[4]

We wish to report that when aldehydes were oxidized with the Caro acid in the presence of alcohols the esters of corresponding acids could be obtained in high yield according to the equation

$$R{-}CHO + H_2SO_5 \xrightarrow{R''OH} RCOOR'' + H_2O + H_2SO_4$$

The results of these oxidations are summarized in Table I.

TABLE I

OXIDATION OF ALDEHYDES IN ALCOHOLS WITH THE CARO ACID

Aldehyde	Alcohol	Product	Conversion, %[a]	Selectivity, %[b]
Methacrolein	Methanol	Methyl methacrylate	94	91[c]
Methacrolein	Methanol	Methyl methacrylate	90	97[d]
Methacrolein	*e*	Methacrylic acid	65	29[d]
Methacrolein	Ethanol	Ethyl methacrylate	100	88[d]
Methacrolein	Isopropyl alcohol	Isopropyl methacrylate	83	55[d]
Acrolein	Methanol	Methyl acrylate	100	85[d]
Crotonaldehyde	Methanol	Methyl crotonate	100	63[d]
Propionaldehyde	Methanol	Methyl propionate	90	97[d]
Benzaldehyde	Methanol	Methyl benzoate	100	100[d]

[a] Conversion (%) = 100 (moles of aldehyde reacted/moles of aldehyde charged). [b] Selectivity (%) = 100 (moles of product/moles of aldehyde reacted). [c] The Caro acid was prepared from $(NH_4)_2S_2O_8$. [d] The Caro acid was prepared from H_2O_2 and H_2SO_4. [e] Ethyl ether was used instead of alcohol.

Mechanistically, it seems plausible that the Baeyer–Villiger reaction occurs first and esterification follows. Thus, the aldehyde is oxidized with the Caro acid to the corresponding carboxylic acid, which is esterified immediately with alcohol. However, when methacrolein was oxidized in ethyl ether instead of in methanol, the conversion of methacrolein and the selectivity of the main oxidation product (methacrylic acid) decreased remarkably. On the other hand, the rate of esterification of methacrylic acid with methanol in the presence of H_2SO_4 is much slower than that of oxidation of methacrolein in methanol with the Caro acid under the same condition of reaction (Figure 1). From these results, the above-mentioned mechanism involving intermediate formation of methacrylic acid followed by esterification could be excluded.

The direct formation of esters by the oxidation of primary alcohols with chromic acid was reported to occur by the reaction sequence, alcohol → aldehyde ⇌ hemiacetal → ester, rather than by the commonly ac-

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(4) Halcon International, Inc., Netherlands Patent Application, 6,412,904 (1965); *Chem. Abstr.*, **63**, 13085e (1965).