Electrophilic Fluorination of Diazoketones

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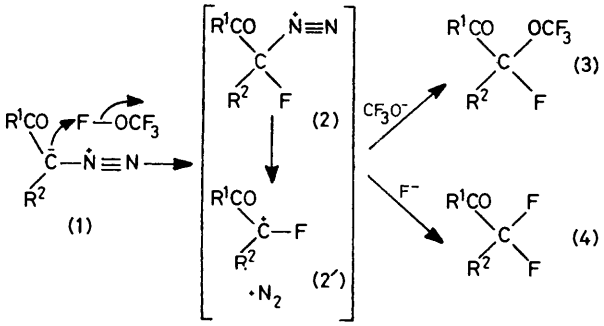
Fluorination of diazoketones with trifluoro(fluoro-oxy)methane produces mainly a mixture of αα-difluoroketones and α-fluoro-α-trifluoromethoxy ketones. The initial electrophilic attack on the diazo group is followed by nucleophilic attack by F^- or CF_3O^-. In the case of diazocamphor a rearrangement occurs and leads to the formation of a fluorotricyclanone. The use of molecular fluorine can also lead to αα-difluoroketones.

FLUORINATION of organic compounds by molecular fluorine is rendered particularly difficult by the high reactivity of this reagent which can break carbon–carbon bonds. Less drastic and more selective fluorinating agents such as trifluoro(fluoro-oxy)methane (CF_3OF) are commonly used. There has been a controversy over the ionic or radical nature of the action of trifluoro-(fluoro-oxy)methane on double bonds. The observed transposition reactions and solvent participation favour an ionic mechanism.[1] However, the fluorination of halogenated olefins by trifluoro(fluoro-oxy)methane is neither regio- nor stereo-selective: this would rather suggest a radical mechanism.[2]

The ionic character of the reagent is best revealed by its action on polar substrates. Thus, we have studied its reactivity on primary and secondary diazoketones. These compounds are known to be particularly sensitive to electrophilic attack by halogens and pseudohalogens.[3] This study shows that the reagent behaves like a pseudo-halogen[4] and its polarization is $F\text{–}\overset{\delta^+ \rightarrow \delta^-}{O}CF_3$. In the presence of a radical inhibitor (such as nitrobenzene),[5] the reaction is not substantially modified. In the case of 3-diazobornan-2-one (3-diazocamphor) (7), there is evidence for a transposition reaction with an ionic intermediate.

Reactions were carried out at −70 °C in an inert solvent (chlorotrifluoromethane) and both αα-difluoro and α-fluoro-α-trifluoromethoxy ketones were always isolated. Nucleophilic attack of the polarized diazoalkanone (1) on the fluorine atom bonded to oxygen is followed by nucleophilic attack by CF_3O^- or F^- (there is an equilibrium, $CF_3O^- \rightleftharpoons COF_2 + F^-$) on an intermediate such as (2) or the resultant α-fluoro-α-oxocarbenium ion (2′) (Scheme 1).

Reactions of Primary Diazoketones with Trifluoro-(fluoro-oxy)methane.—For primary diazoketones, the conversion is generally total (with *ca.* 1.5 equiv. of CF_3OF), however the yields of isolated products are low owing to their difficult separation by methods other than



a; R^1 = Ph, R^2 = H
b; R^1 = C_6H_{11} R^2 = H
c; R^1 = Bu^t, R^2 = H
d; R^1 = $PhCH_2$, R^2 = H
e; R^1R^2 =

SCHEME 1

g.l.c. In the cases of diazoketones (1b—d), the reaction leads to the formation of ketones (3) and (4) as well as to two different epoxides (5) and (6), which have been isolated for cases (1b and c) and/or characterized, especially by n.m.r. spectrography. Compounds of type (5) have two vicinal fluorines. Compounds (6) have vicinal fluorine and trifluoromethoxy groups. The n.m.r. spectra of both types of epoxides display geminal H–F coupling constants (85 Hz) as observed in monofluorinate-epoxides.[6] These compounds can result from an attack

[1] (*a*) D. H. R. Barton, L. S. Godinho, R. H. Hesse, and M. M. Pechet, *Chem. Comm.*, 1968, 804; (*b*) D. H. R. Barton, L. J. Banks, A. K. Ganguly, R. H. Hesse, G. Tarzia, and M. M. Pechet, *ibid.*, 1969, 227; (*c*) D. H. R. Barton, R. H. Hesse, G. P. Jackman, L. Ogunkoya, and M. M. Pechet, *J.C.S. Perkin I*, 1974, 739.

[2] K. Johri and D. D. Des Marteau, Third Winter Fluorine Conference, St. Petersburg, Florida, 1977.

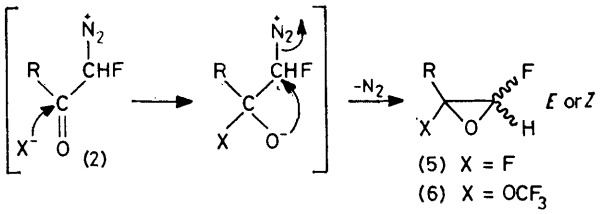
[3] (*a*) O. O. Orazi, R. A. Corral, and H. Schuttenberg, *J.C.S. Perkin I*, 1974, 2087 and references therein; (*b*) G. A. Olah and J. Welch, *Synthesis*, 1974, 896 and references therein.

[4] Preliminary communication, C. Wakselman and J. Leroy, *J.C.S. Chem. Comm.*, 1976, 611.

[5] D. H. R. Barton, R. H. Hesse, R. E. Markwell, M. M. Pechet, and H. T. Toh, *J. Amer. Chem. Soc.*, 1976, **98**, 3034.

[6] E. Elkik and M. Le Blanc, *Bull. Soc. chim. France*, 1971, 870.

of the trifluoromethoxide anion or fluoride anion on the carbonyl group of the α-oxodiazonium ion (2) (Scheme 2).



SCHEME 2

Since the reaction leads to one isomer only, it is not likely that a genuine α-oxocarbenium ion (2′) is formed. If that were so, the reaction would yield a mixture of *cis*- and *trans*-isomers for each epoxide. Asymmetric induction seems more likely, either on (1) and/or (2). A four- or six-centred concerted transfer of trifluoro(fluoro-oxy)methane (CF_3O–F or F–CF_2O–F) to the diazoketone cannot be completely discarded.

The stereochemistry of the two types of epoxides could not be determined from the proton–fluorine or fluorine–fluorine coupling constants. However, in the case of epoxides (6), the value of the fluorine–fluorine coupling constant increases with the size of the substituent R. This would favour fluorine and trifluoromethoxy *cis* relative to the epoxide plane. The coupling would be through space and would increase with the steric interaction between R and the trifluoromethoxy group.

The percentages of the various fluorination products measured by ^{19}F n.m.r. spectrography are listed in Table 1.

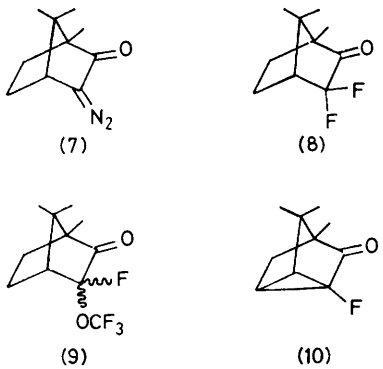
TABLE 1

Product distribution for the addition of trifluoro(fluoro-oxy)methane to primary diazoketones(1)

	Product (%)			
Substrate	(3)	(4)	(5)	(6)
(1a)	42	58	0	0
(1b)	25	43	20	12 [b]
(1c)	27	32	30	11
(1c) [a]	29	32	25	14
(1d)	24	40	27 [c]	9 [c]

[a] With 0.1 equiv. $PhNO_2$ added. [b] Isolated impure. [c] Not isolated.

Reaction of 3-Diazobornan-2-one with Trifluoro(fluoro-oxy)methane.—The acid-catalysed decomposition of secondary α-diazoketones, and particularly of 3-diazobornan-2-one (7), has shown that the products depend (i) on the structure of the diazonium ion (2), (ii) on thermodynamic *versus* kinetic control of the formation of the epimeric diazonium ions, and (iii) on the solvent system in which the reaction takes place. It is generally accepted that there is no α-oxocarbenium ion (2′) formed by loss of nitrogen. On the contrary, there is concerted loss leading to the formation of different non-classical ions according to whether the diazonium ion (2) is of *exo*- or *endo*-type.[7] Thus, there are many products corresponding to the various sites which can be attacked by the counterion. However, in the case of the reaction of 3-diazobornan-2-one with trifluoro(fluoro-oxy)methane, the composition of the crude product is simpler as shown by its ^{19}F n.m.r. spectrum. Nevertheless, two signals which are probably trifluoromethoxy resonances and are not associated with fluorine resonances have not been assigned. The other signals are from three compounds which have been isolated by g.l.c. in the ratio 31 : 27 : 42 (the total yield with respect to diazobornan-2-one is 60%). The structure of these compounds has been determined mainly by n.m.r. spectroscopy. The large value for the fluorine–fluorine coupling constant in 3,3-difluorobornan-2-one (8) is an unambiguous indication of geminal difluoro substitution. At 250 MHz, the most shielded methyl resonance



(δ 1.22) is a doublet (*J* 5.5 Hz). This is probably the 8-methyl resonance with through-space coupling with the *exo*-fluorine atom. The *endo*-fluorine resonance is a singlet and this nucleus is therefore not coupled with any of the neighbouring protons such as 4-H.

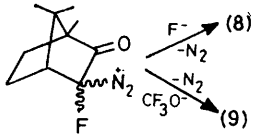
Compound (9) is a mixture of two isomers in the ratio 66 : 34. The ^{19}F n.m.r. spectrum of this mixture displays resonances for the two trifluoromethoxy groups and also for the corresponding fluorine atoms substituted on a tertiary carbon atom. There are no ^1H n.m.r. resonances with chemical shifts up to δ 2.8; this excludes a $CH(OCF_3)$ group.

The ^{19}F n.m.r. spectrum of 2-fluoro-4,7,7-trimethyltricyclo[2.2.1.$0^{2,6}$]hept-3-one (10) has a triplet to high field of $CFCl_3$ [δ 234 ($CDCl_3$)]. Its ^1H n.m.r. spectrum ($CDCl_3$) displays distinct signals for the three methyl groups. One at high field is a doublet. Two resonances, δ 1.94 and 2.33, are both doublets (respectively *J* 2 and 10.6 Hz). At 250 MHz, this pattern is unchanged. By heteronuclear decoupling of the fluorine atom, all the doublets become singlets. As in the case of 3,3-difluorobornan-2-one (8), it is probable that the fluorine atom is coupled through space with the 8-methyl group protons. Furthermore, 1- and 6-H appear to be equivalent (δ 2.33); the same applies to *exo*-5- and *endo*-5-H (δ 1.94). These nuclei are coupled only to fluorine. The structure of compound (10) was confirmed by its ^{13}C n.m.r. spectrum which exhibits characteristic cyclopropane ^{13}C–F couplings.

The reaction of trifluoro(fluoro-oxy)methane with 3,3-difluorobornan-2-one can be compared with that of

[7] L. Friedman, ' Carbonium Ion Formation From Diazonium Ions ' in ' Carboniums Ions,' Wiley, New York, 1970, p. 692.

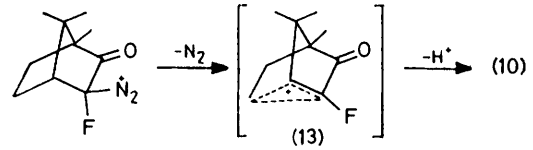
hydrogen chloride in an aprotic solvent where the rearrangement is limited to the formation of a tricyclic compound.[8] The formation of the geminal compounds (8) and (9) can be explained in terms of an S_N2 displace-



(12)

ment of nitrogen by the counterions CF_3O^- or F^- acting on the α-fluorodiazonium ions (12). The dispersion of the counterions in the medium is limited by use of a non-polar solvent.

Cyclopropanation, which leads to the formation of product (10), results from the loss of a proton from one of the ions (13) resulting from rearrangement of the



exo – (12)

exo-diazonium ion (12). In the case of ion (12), the loss of nitrogen is favoured by assistance of the C(4)–C(5) bond which is antiparallel to the C(3)–N bond.

Reactions of Fluorine with Diazoketones.—A survey of the literature shows that non-selective fluorination would be expected together with polyfluorination and carbon–carbon bond breaking. However, although elemental fluorine can have a regiospecific action on saturated carbon,[5,9] earlier work shows that alkyl chains and phenyl are inert under similar conditions.[10]

At −70 °C, molecular fluorine diluted by an inert gas reacts with aliphatic diazoketones (1a—c) in chlorotrifluoromethane solutions. As expected, the reaction yields the corresponding α-difluoro-ketones. The ^{19}F n.m.r. spectrum of the crude products shows clearly the resonance of geminal fluorines among numerous, unidentified fluorine signals. Difluoro-ketone (4c) was isolated in low yield (15%).

$$Bu^tCOCHN_2 \xrightarrow[CFCl_3]{F_2} Bu^tCOCHF_2 + \text{fluorinated by-products}$$
(4c)

Under the same conditions, 3,3-difluoronorbornan-2-one (8) was fluorinated to give a complex mixture from which compounds (8) and (10) could be isolated in the ratio 70 : 30. Nevertheless, yields remained low.

In conclusion, the study of the reaction of trifluoro-(fluoro-oxy)methane with α-diazoketones shows that an ionic mechanism is involved. This type of mechanism is probably predominant when trifluoro(fluoro-oxy)-methane is in the presence of a highly polarised substrate. The mode of reaction of molecular fluorine is not very well known,[9,11] but it is shown here that fluorine reacts with diazoketones as an electrophile.

EXPERIMENTAL

^1H (60 MHz; Me_4Si as internal standard) and ^{19}F n.m.r. spectra (56.4 MHz; $CFCl_3$ as internal standard) were recorded with a JEOL C-60 HL instrument equipped with JEOL JNM-SD-HC heteronuclear spin decoupler. Spectra at 250 MHz were obtained with a Cameca spectrometer. ^{13}C N.m.r. spectra were run at 20 MHz with a Varian CFT-20 spectrometer. I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer for solutions in carbon tetrachloride. Mass spectra were obtained at 70 eV on an A.E.I.-MS 30 double beam apparatus. Preparative g.l.c. were performed with a Varian Aerograph model 920 chromatograph [columns: Apiezon L (15%)–Chromosorb WAW 60/80 (2 m); SE30 (30%)–Chromosorb PAW 45/60 (3 m); and

TABLE 2

N.m.r. data (δ; $CDCl_3$) for fluorinated products obtained from primary diazoketones (1)

Product	^1H	^{19}F
(3a)	6.34 (1 H, d, $J_{H,F}$ 56 Hz, CHF), 7.23—8.12 (5 H, m, Ph)	60.2 (3 F, d, $J_{F,F}$ 4.9 Hz, OCF_3), 135.5 (1 F, dqt, $J_{F,H}$ 0.9 Hz, CHF)
(4a)	6.23 (1 H, t, $J_{H,F}$ 53 Hz, CHF_2), 7.2—8.17 (5 H, m, Ph)	123.7 (dt, $J_{F,H}$ 1.0 Hz, CHF_2)
(3b)	0.48—2.52 (10 H, m), 2.82 (1 H, m), 5.76 (1 H, d, $J_{H,F}$ 56.0 Hz, CHF)	60.7 (3 F, d, $J_{F,F}$ 4.6 Hz, OCF_3), 138.2 (1 F, dqd, $J_{F,H}$ 1.6 Hz, CHF)
(4b)	0.57—2.53 (10 H, m), 2.82 (1 H, m), 5.68 (1 H, t, $J_{H,F}$ 53.6 Hz, CHF_2)	128.6 (dd, $J_{F,H}$ 1.2 Hz, CHF_2)
(3c)	1.28 (9 H, $J_{H,F}$ 0.8 Hz, CH_3), 6.08 (1 H, d, $J_{H,F}$ 56.5 Hz, CHF)	61.5 (3 F, d, $J_{F,F}$ 4.7 Hz, OCF_3), 137.5 (1 F, dqm, CHF)
(4c)	1.28 (9 H, t, $J_{H,F}$ 0.75 Hz, CH_3), 5.98 (1 H, t, $J_{H,F}$ 53.5 Hz, CHF_2)	126.8 (d, CHF_2)
(3d)	3.89 (2 H, d, $J_{H,F}$ 1.5 Hz), 5.89 (1 H, d, $J_{H,F}$ 56 Hz, CHF), 7.2 (5 H, Ph)	60.0 (3 F, d, $J_{F,F}$ 4.9 Hz, OCF_3), 137.5 (1 F, dqt, CHF)
(4d)	3.82 (2 H, t, $J_{H,F}$ 1.1 Hz, CH_2), 5.58 (1 H, t, $J_{H,F}$ 53.6 Hz, CHF_2), 7.2 (5 H, Ph)	127.6 (dt, CHF_2)
(5; R = C_6H_{11})	0.58—2.63 (11 H, m), 5.31 (1 H, dd, $J_{H,F}$ 84.0, 2.2 Hz, CHF)	152.0 (1 F, ddd, $J_{F,F}$ 35.3 Hz, $J_{F,H}$ 12.0 Hz, CFR), 163.5 (1 F, dd, CHF)
(6; R = C_6H_{11})[a]	5.48 (d, $J_{H,F}$ 84.0 Hz, CHF)	54.8 (3 F, d, $J_{F,F}$ 3.9 Hz, OCF_3), 163.0 (1 F, dqd, $J_{F,H}$ 1.7 Hz, CHF)
(5; R = Bu^t)	1.07 (9 H, d, $J_{H,F}$ 0.8 Hz, CH_3), 5.45 (1 H, dd, $J_{H,F}$ 85.0, 2.5 Hz, CHF)	155.5 (1 F, dm, $J_{F,F}$ 36.0 Hz, CFR), 163.0 (1 F, dd, CHF)
(6; R = Bu^t)	1.04 (9 H, s, CH_3), 5.48 (1 H, d, $J_{H,F}$ 85.0 Hz, CHF)	53.6 (3 F, d, $J_{F,F}$ 8.8 Hz, OCF_3), 163.1 (1 F, dq, CHF)

[a] Isolated impure.

[8] M. Hanack and J. Dolde, *Tetrahedron Letters*, 1966, 321.

[9] D. H. R. Barton, R. H. Hesse, R. E. Markwell, M. M. Pechet, and S. Rozen, *J. Amer. Chem,. Soc.*, 1976, **98**, 3036.

[10] R. H. Merritt and F. A. Johnson, *J. Org. Chem.*, 1967, **32**, 416.

[11] R. Breslow, R. J. Corcoran, B. B. Snider, R. J. Doll, P. L. Khanna, and R. Kaleya, *J. Amer. Chem. Soc.*, 1977, **99**, 905.

EGS (15%)-Chromosorb WAW 60/80 (2 m); He as carrier gas]. B.p.s were determined by Siwoloboff's method on a Büchi apparatus and m.p.s on the same apparatus. Trifluoro(fluoro-oxy)methane was supplied by Société des Usines Chimiques de Pierrelatte. Aliphatic diazoketones were prepared from the corresponding acid chlorides by Eistert's method and 3-diazobornan-2-one by the method of Cava *et al.*[12]

Fluorinations of Diazoketones with Trifluoro(fluoro-oxy)-methane.—General procedure. Diazoketone (15—65 mmol) in trichlorofluoromethane (150 ml) [for (1a), chloroform (50 ml) was added to maintain solubility at low temperature] at −70 °C was stirred while an excess (1.5 equiv.) of trifluoro(fluoro-oxy)methane diluted to 20% with nitrogen was bubbled in. The mixture was allowed to warm to room temperature under nitrogen. The solution was neutralised with a 5% sodium hydrogencarbonate solution and extracted with trichlorofluoromethane. The combined extracts were washed with brine and dried ($MgSO_4$). After rotary evaporation or distillation at atmospheric pressure [case (1c)], the resulting mixture was separated by preparative g.l.c. after bulb-to-bulb distillation under reduced pressure.

α-Fluoro-α-trifluoromethoxyacetophenone (3a) (yield 10% from acid chloride) had b.p. 182—183° at *ca.* 760 Torr; $\nu_{max.}$ 1 722—1 702 cm^{-1} (Found: C, 48.75; H, 2.8; F, 34.2. $C_9H_6F_4O_2$ requires C, 48.65; H, 2.7; F, 34.2%); *m/e* 222 (M^+). *α,α-Difluoroacetophenone* (14%) had b.p. 185° at *ca.* 760 Torr; $\nu_{max.}$ 1 714—1 701 cm^{-1} (Found: C, 61.7; H, 3.9; F, 24.35. $C_8H_6F_2O$ requires C, 61.55; H, 3.85; F, 24.35%); *m/e* 156 (M^+). *Cyclohexyl fluoro(trifluoromethoxy)methyl ketone* (3b) (9%) had b.p. 172—173° at *ca.* 760 Torr; $\nu_{max.}$ 1 735 cm^{-1} (Found: C, 47.8; H, 5.45; F, 33.05. $C_9H_{12}F_4O_2$ requires C, 47.35; H, 5.3; F, 33.3%); *m/e* 228 (M^+). *Cyclohexyl difluoromethyl ketone* (4b) (14%) had b.p. 168° at *ca.* 760 Torr; $\nu_{max.}$ 1 733 cm^{-1} (Found: C, 59.3; H, 7.5; F, 23.55. $C_8H_{12}F_2O$ requires C, 59.25; H, 7.45; F, 23.45%); *m/e* 162 (M^+). *Difluoromethyl t-butyl ketone* (4c) (12%) had b.p. 103—104° at *ca.* 760 Torr; $\nu_{max.}$ 1 740sh, 1 736sh, and 1 723 cm^{-1} (Found: C, 53.0; H, 7.15; F, 27.9. $C_6H_{10}F_2O$ requires C, 59.25; H, 7.4; F, 27.9%). *Fluoro(trifluoromethoxy)methyl t-butyl ketone* (11%) had b.p. 116—117° at *ca.* 760 Torr; $\nu_{max.}$ 1 744—1 726 cm^{-1} (Found: C, 41.65; H, 4.95; F, 37.5. $C_7H_{10}F_4O_2$ requires C, 41.6; H, 5.0; F, 37.6%). 1,2-*Difluoro-1-t-butyloxiran* (5; R = Bu^t) was formed in 6% yield (Found: C, 52.3; H, 7.2. $C_6H_{10}F_2O$ requires C, 52.95; H, 7.4%). 2-*Fluoro-1-t-butyl-1-trifluoromethoxyoxiran* was formed in 5% yield (Found: C, 41.4; H, 5.15. $C_7H_{10}F_4O_2$ requires C, 41.6; H, 5.0%). Benzyl fluoro(trifluoromethoxy)methyl ketone (3d) (6%) had b.p. 197° at *ca.* 760 Torr; m.p. 78—79°; $\nu_{max.}$ 1 754 cm^{-1}; *m/e* 236 (M^+). Benzyl difluoromethyl ketone (8%), b.p. 203° at *ca.* 760 Torr; $\nu_{max.}$ 1 754 cm^{-1}; *m/e* 170 (M^+).

Reaction of 3-Diazobornan-2-one with Trifluoro(fluoro-oxy)-methane.—3-Diazobornan-2-one (7) (3.6 g, 20 mmol) was treated with trifluoro(fluoro-oxy)methane (1.5 equiv.) as described above. The components of the crude product (oil; 4.2 g) were separated by g.l.c. on an EGS column, giving in order of elution *3-fluoro-3-trifluoromethoxybornan-2-one* (9) (0.82 g, 16%) as a mixture of epimers (liquid), $\nu_{max.}$ 1 782 cm^{-1}; $\delta_H(CDCl_3)$ 0.92—1.18 (9 H, CH_3) and 0.6—3.0 (5 H, m, CH and CH_2); $\delta_F(CDCl_3)$ one epimer (66%) 52.8 (3 F, dd, $J_{F,F}$ 9.4, $J_{F,H}$ 1.8 Hz, OCF_3) and 113 (1 F, m, $W_{1/2}$ 29.6 Hz, CF); other epimer (34%) 53.7 (3 F, dd, $J_{F,F}$ 9.5, $J_{F,H}$ 1.5 Hz, OCF_3) and 115.4 (1 F, q, CF) (Found: C, 51.7; H, 5.5; F, 29.85. $C_{11}H_{14}F_4O_2$ requires C, 51.95; H, 5.55; F, 29.9%); *m/e* 254 (M^+); *3,3-difluorobornan-2-one* (8) (purified by sublimation at 0.01 Torr) (0.71 g, 19%), m.p. (sealed capillary) 175—177°; $\nu_{max.}$ 1 775 cm^{-1}; $\delta_H(CDCl_3)$ (250 MHz) 0.6—2.6 (5 H, m, CH and CH_2), 1.22 (3 H, d, $J_{H,F exo}$ 6 Hz, CH_3), 1.23 (3 H, s, CH_3), and 1.30 (3 H, s, CH_3); $\delta_F(CDCl_3)$ 109.3 (1 F, dm, $J_{F,F}$ 280, $W_{1/2}$ 18.3 Hz, F *exo*) and 115.5 (1 F, d, F *endo*) (Found: C, 63.9; H, 7.3; F, 20.5. $C_{10}H_{14}F_2O$ requires C, 63.8; H, 7.5; F, 20.2%); *m/e* 188 (M^+); and *2-fluoro-4,7,7-trimethyltricyclo*[2.2.1.$0^{2,6}$]*heptan-3-one* (10) (purified by sublimation at 0.01 Torr) (0.86 g, 25%), m.p. (sealed capillary) 142—144°; $\nu_{max.}$ 1 769 cm^{-1}; $\delta_H(CDCl_3)$ 0.81 (3 H, d, $J_{H,F}$ 1.4 Hz, CH_3), 0.93 (3 H, s, CH_3), 1.00 (3 H, s, CH_3), 1.94 (2 H, d, $J_{H,F}$ 2 Hz, *exo*- and *endo*-5-H), and 2.33 (2 H, d, $J_{H,F}$ 10.6 Hz, 1- and 6-H); $\delta_H(C_6D_6)$ 0.52 (3 H, s, CH_3), 0.63 (3 H, d, $J_{H,F}$ 1.3 Hz, CH_3), 0.76 (3 H, s, CH_3), 1.46 (2 H, d, $J_{H,F}$ 1.9 Hz, *exo*- and *endo*-5-H), and 1.87 (2 H, d, $J_{H,F}$ 10.6 Hz, 1- and 6-H); $\delta_F(CDCl_3)$ 234 (t, $J_{F,H}$ 10.6 Hz, CF); $\delta_C(C_6D_6$; $Me_4Si)$ 6.02 (s, C-10), 19.71 (s, C-8 or -9), 20.97 (s, C-9 or -8), 24.3 (d, $J_{C,F}$ 7.1 Hz, C-1 or -6), 35.9 (s, C-5), 36.5 (d, $J_{C,F}$ 6.0 Hz, C-6 or -1), 44.1 (s, C-7), 49.6 (s, C-4), 82.6 (d, $J_{C,F}$ 270.5 Hz, C-2), and 186.5 (d, $J_{C,F}$ 8.1 Hz, C-3) (Found: C, 71.3; H, 7.8; F, 11.75. $C_{10}H_{13}FO$ requires C, 71.4; H, 7.75; F, 11.3%); *m/e* 168 (42%, M^+), 153 (22, $M - CH_3^+$), and 125 [100, $M - (CH_3 + CO)^+$].

Reaction of 1-Diazo-3,3-dimethylbutan-2-one with Fluorine.—Diazoketone (1c) (80 mmol) in chlorotrifluoromethane (300 ml) was stirred vigorously at −65 °C while an excess of fluorine (*ca.* 1.5 equiv.) diluted to 10% in nitrogen was passed through until the solution became colourless. The mixture was purged with nitrogen, allowed to warm to room temperature, and then worked-up as described for trifluoro(fluoro-oxy)methane. Distillation gave the ketone (1.5 g, 14%).

Reaction of 3-Diazobornan-2-one with Fluorine.—Diazoketone (7) (3.7 g, 20 mmol) treated by fluorine as described above gave an oil (4.1 g) which was chromatographed on Merck silica gel 60 (benzene as eluant). An unidentified oil was first eluted, then 3,3-difluorobornan-2-one (8) followed by tricyclanone (10). Compounds (8) and (10) were purified by repeated preparative g.l.c.–sublimation and identified by comparison with compounds obtained from trifluoro(fluoro-oxy)methane.

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