
Fluorocarbon and Related
Chemistry— Volume 3

Specialist Periodical Reports

The Chemical Society

A Specialist Periodical Report

Fluorocarbon and Related Chemistry

Volume 3

A Review of the Literature Published during
1973 and 1974

Senior Reporters

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Preface

This is the third volume in a series of biennial reviews concerned with the chemistry of organic, organometallic, and organometalloidal compounds of the fluorocarbon class and of their polyfluorinated analogues. As in the previous volumes (referred to throughout as Vol. 1 and Vol. 2), compounds containing a low proportion of C—F bonds are mentioned only when relevant to the main theme. Unlike the previous volumes, this one contains no chapter dealing with selected progress in n.m.r. spectroscopy, an item this time considered to be too much of a luxury in view of the nature of the relevant information published and space limitations imposed by financial considerations. Otherwise, the style is unaltered, great efforts having been made to provide essentially comprehensive articles containing a good proportion of visual aids in the form of reaction schemes and compound structures; again, limited overlap between chapters coupled with cross-referencing offsets to some extent the absence of a subject index, provision of which would price this book out of the market. The *F*-system of nomenclature, whereby, for example, $\text{CF}_3\cdot\text{CF}:\text{CF}_2$ is named *F*-propene, $\text{CF}_3\cdot\text{O}\cdot\text{CH}:\text{CH}_2$ *F*-methyl vinyl ether, and $\text{CHF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CF}_2\cdot\text{CH}_2\cdot\text{OH}$ 1,1,6-trihydryl-*F*-hexan-1-ol, recently adopted by the American Chemical Society (see J. A. Young, *J. Chem. Documentation*, 1974, **14**, 98) has *not* been used in preference to perfluoro terminology.

The Reporters who helped to produce Vol. 2 have given of their best once more, and we have been ably assisted also by two other colleagues, Tony Tipping and Vic Davis, whose services were sought when it became obvious that the pile of literature to be dealt with would reach a record size for a two-year period. We are indeed deeply indebted to all our Reporters and to our Departmental Librarian, David Whitehurst, for invaluable assistance with literature searching so unselfishly given, and Mike Amor for some proof-reading. All of us owe an enormous debt of gratitude to Mrs. Joan Colclough for the amazingly efficient manner in which she converted our manuscripts into virtually fault-free typescripts.

September 1975

R.E.B.
M.G.B.

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Saturated Fluorocarbons, Fluorocarbon Hydrides, and Fluorocarbon Halides

BY R. E. BANKS

1 Fluorocarbons

More information concerning the preparation,¹⁻⁴ properties,^{1, 5-7} and applications⁸ (lubricants, seals, and bearings;⁹ cathode components for high-energy batteries;¹⁰ g.s.c. stationary phase;¹¹ precursor of diamonds and fluorinated diamonds¹²) of poly(carbon monofluoride) ('graphite fluoride') is now available. Detailed experimental procedures for the direct fluorination of regular or pyrolytic graphite using autoclave, fluidized-bed, or normal flow techniques are now to hand;¹ production of snow-white superstoichiometric poly(carbon monofluoride), $[\text{CF}_{1.12 \pm 0.03}]_n$, by

- ¹ R. J. Lagow, R. B. Badachhape, J. L. Wood, and J. L. Margrave, *J.C.S. Dalton*, 1974, 1268 (preliminary communication: *J. Amer. Chem. Soc.*, 1974, **96**, 2628). Instructions for the synthesis of 'tetracarbon monofluoride' from graphite, fluorine, and hydrogen fluoride (see Vol. 2, p. 2) are reiterated in this paper.
- ² J. Maire, J. M. Martinet, and R. Ruauux, *Fr. P.* 2 126 595/1972 (*Chem. Abs.*, 1973, **79**, 5869f).
- ³ N. Watanabe, M. Takashima, and Y. Kita, *Nippon Kagaku Kaishi*, 1974, 885 (*Chem. Abs.*, 1974, **81**, 42 024p).
- ⁴ T. Kanemaru, T. Shimada, and I. Inudow, *Ger. Offen.* 2 306 737/1973 (*Chem. Abs.*, 1973, **79**, 147 832n).
- ⁵ A. J. Valerga, R. B. Badachhape, G. D. Parks, P. Kamarchik, and J. L. Wood, *U.S. Nat. Tech. Inform. Serv., AD Reports*, 1974, No. 776 990/4GA (*Chem. Abs.*, 1974, **81**, 69 310r) (thermodynamic data and surface-area measurements).
- ⁶ L. B. Ebert, J. I. Brauman, and R. A. Huggins, *J. Amer. Chem. Soc.*, 1974, **96**, 7841.
- ⁷ V. K. Mahajan, R. B. Badachhape, and J. L. Margrave, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 1103.
- ⁸ For reviews, see T. Ishikawa and Y. Takeda, *Kagaku Kogyo*, 1973, **24**, 189 (*Chem. Abs.*, 1973, **78**, 100 015n); N. Watanabe and M. Takashima, *Yuki Gosei Kagaku Kyokai Shi*, 1973, **31**, 455; and N. Watanabe, *Denki Kagaku*, 1972, **40**, 547 (*Chem. Abs.*, 1973, **79**, 37 884y, 13 6014w).
- ⁹ H. Ukihashi and K. Kirimoto, *Japan. P.* 73 38 444 (*Chem. Abs.*, 1974, **81**, 66 114u); S. Kurosaki and Y. Okamoto, *Japan. Kokai* 73 49 827 (*Chem. Abs.*, 1973, **79**, 142 351v); T. Hiratsuka and T. Shimada, *U.S.P.* 3 717 576/1973 (*Chem. Abs.*, 1973, **78**, 125 469b); H. Takeuchi, Y. Okamoto, S. Kurosaki, and K. Nakamoto, *U.S.P.* 3 756 925/1973 (*Chem. Abs.*, 1974, **80**, 29 109e); J. T. Martin, *U.S.P.* 3 765 929/1973 (*Chem. Abs.*, 1974, **80**, 39 960q); S. Kurosaki and Y. Okamoto, *U.S.P.* 3 787 294/1974 (*Chem. Abs.*, 1974, **80**, 140 593x); M. Saito, S. Kurosaki, K. Naito, and F. Yamaguchi, *Japan. Kokai*, 74 27 443 (*Chem. Abs.*, 1974, **81**, 81 234b).
- ¹⁰ M. Fukuda, *Japan. P.* 73 26 891, 26 892, 26 893 (*Chem. Abs.*, 1974, **80**, 90 396n, 90 397p, 90 398q).
- ¹¹ L. G. Swope and E. A. Smith, Report 1972, GAT-T-1903 (*Chem. Abs.*, 1973, **79**, 73 171x) (a g.c. column packed with $[\text{CF}_x]_n$ was found especially useful for analysis of air-F₂-Cl₂-ClF-ClF₃ mixtures); see also V. F. Palfitov, A. I. Loskutov, I. A. Kuzin, and V. N. Knott, *Kolloid. Zhur.*, 1974, **36**, 802 (*Chem. Abs.*, 1974, **81**, 176 660b).
- ¹² J. L. Margrave, R. G. Bautista, P. J. Ficalora, and R. B. Badachhape, *U.S.P.* 3 711 595/1973. Defluorination of $[\text{CF}_{1.12}]_n$ with powdered Mg at 700 °C and 20 000 atm yields a mixture of diamonds and fluorinated diamonds; the same conversion can be effected with Al or Ni, and polytetrafluoroethylene may be used instead of poly(carbon monofluoride).

the flow or fluidized-bed method demands a reaction temperature range of $627 \pm 3^\circ\text{C}$, outside which either carbon tetrafluoride plus soot (at $> 630^\circ\text{C}$) or black-to-grey substoichiometric material (*e.g.* black $[\text{CF}_{0.68}]_n$ at 540°C) are formed. At atmospheric pressure, fluorine does not appear to attack graphite at temperatures below 450°C , but at pressures greater than 225 lbf in^{-2} , reaction occurs spontaneously at 20°C and can lead to a violent explosion if the rate of introduction of fluorine into the autoclave is not regulated carefully.^{1,13} No decomposition of superstoichiometric poly(carbon monofluoride) appears to occur at $650\text{--}700^\circ\text{C}$ in the presence of fluorine.¹⁴ More structural data for poly(carbon monofluoride) are available following an X-ray powder diffraction study¹⁴ on material pressed at 20 kbar and 150°C and determination of the n.m.r. absorption mode second moment of commercial Fluorographite samples (see Vol. 2, p. 1, ref. 2) of stoichiometry $\text{CF}_{1.06}$ and $\text{CF}_{1.15}$;¹⁵ the results of the latter study indicate that the most plausible layer structure comprises an infinite array of *cis-trans*-linked cyclohexane boats.

Direct fluorination (flow method) of 'graphite oxide', $[\text{C}_8\text{O}_2(\text{OH})_2]_n$ (from graphite/ $\text{KMnO}_4\text{--NaNO}_3\text{--H}_2\text{SO}_4$ at 66°C) at 20°C and 1 atm yields a powdery, pale grey, thermally (above 50°C) and hydrolytically unstable 'oxyfluoride' {16.25—22.4% F; λ_{max} 1095 cm^{-1} (C—F stretch); *cf.*¹ $[\text{C}_4\text{F}]_n$ 1090 cm^{-1} , $[\text{CF}_{1.12 \pm 0.03}]_n$ 1217s ($\rightarrow\text{C—F}$), 1342m , 1072w (peripheral CF_2) cm^{-1} }.¹

Full details have been published of the direct fluorination of hydrocarbon polymers¹⁶ by the so-called LaMar procedure,^{17–19} the principal feature of which is infinite dilution initially with helium or nitrogen followed by gradient changes of fluorine concentration; with substrate particle sizes greater than 100 mesh a hydrocarbon core is retained, and large fabricated items such as polyethylene bottles can

¹³ For discussions of the high-temperature kinetics of pyrolytic graphite gasification by fluorine, the adsorption of fluorine on graphite, and the production of carbon tetrafluoride from fluorine and graphite, see D. E. Rosner and J. P. Strakey, *J. Phys. Chem.*, 1973, **77**, 690; N. Watanabe, H. Takenaka, and M. Takashima, *Nippon Kagaku Kaishi*, 1973, 487 (*Chem. Abs.*, 1973, **78**, 151 909q); and T. Kanamaru and T. Shimada, Japan. Kokai 74 70 909 (*Chem. Abs.*, 1974, **81**, 151 508v), respectively.

¹⁴ V. K. Mahajan, R. B. Badachhape, and J. L. Margrave, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 1103.

¹⁵ L. B. Ebert, J. I. Brauman, and R. A. Huggins, *J. Amer. Chem. Soc.*, 1974, **96**, 7841.

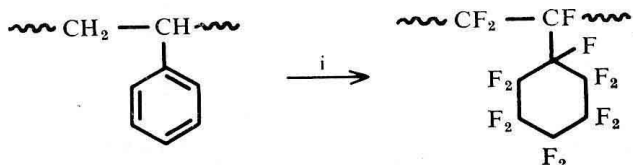
¹⁶ For a review of postpolymerization fluorination techniques, consult B. G. Willoughby, *RAPRA Members Journal*, 1974, 214. See also Z. N. Nudelman and I. P. Prokudin, Belg. P. 800 378/1973 (*Chem. Abs.*, 1974, **81**, 122 418k); T. Kato, Japan. P. 72 47 854, 47 855, 47 856, 73 24 825, 24 826 (*Chem. Abs.*, 1974, **80**, 60 590d, 71 677p, 71 676n, 96 839f, 96 840z) (surface modification of polyethylene using SF_6 -high-energy radiation); J. P. Manion and D. J. Davies, U.S.P. 3 740 256/1973, 3 740 325/1973 (*Chem. Abs.*, 1973, **79**, 55 190y, 54 321e) (surface fluorination of polyethylene, paper, textiles, *etc.* using CF_4 -electrodeless discharge); D. W. Brown, R. E. Florin, and L. A. Wall, *Appl. Polym. Symp.*, 1973, No. 22, p. 169 (*Chem. Abs.*, 1974, **80**, 71 318x) (cross-linking of H-containing fluoropolymers with $\text{F}_2\text{--He}$ at 25°C and 1 atm); R. N. Haszeldine and R. Rowland, U.S.P. 3 816 286/1974 (*Chem. Abs.*, 1974, **81**, 49 245v) (u.v.-initiated 'insertion' of perfluoropropene into backbone or pendant C—H bonds); W. R. Siegart, R. C. Suber, W. D. Blackley, and J. G. Dadura, U.S.P. 3 806 455/1974 [preparation of lubricating oils *via* partial fluorination of polystyrene or polypropylene (*cf.* U.S.P. 3 380 983/1968)]; D. D. Dixon, Ger. Offen. 2 247 615/1973 (*Chem. Abs.*, 1973, **78**, 160 840n) (direct fluorination of Dacron).

¹⁷ (a) R. J. Lagow and J. L. Margrave, *J. Polymer Sci., Polymer Letters*, 1974, **12**, 177; (b) *Chem. and Eng. News*, 1970, **48**, Jan. 12, p. 40

¹⁸ J. L. Margrave and R. J. Lagow, U.S.P. 3 775 489/1973 (*cf.* ref. 17b).

¹⁹ A. J. Otsuka and R. J. Lagow, *J. Fluorine Chem.*, 1974, **4**, 371.

be given a fluorocarbon skin of thickness *ca.* 0.2 mm.^{17,20} Complete, or almost complete, fluorination of finely powdered (<100 mesh) polyethylene,¹⁷ polypropylene,¹⁷ poly(ethylene-co-propylene),¹⁷ polyisobutylene,¹⁹ polyacrylonitrile,¹⁷ polystyrene,^{17,18} and poly-*p*-xylylene¹⁹ can readily be achieved at room temperature, the nitrile $\{-[CF_2 \cdot CF(CF_2 \cdot NF_2)]_n\}$ and benzenoid polymers undergoing fluorine addition as well as hydrogen substitution (see Scheme 1); polyacrylamide¹⁷ and phenol-formaldehyde resins or prepolymers (resols, novolacs)^{17,19} seem to suffer cleavage of pendant groups whilst undergoing change to fluorocarbon systems, and all the linear polymers appear to become cross-linked.



Reagent: i, F₂, 20 °C.

Scheme 1

Instructions for the conversion of polynuclear arenes (coronene, anthracene, decacyclene, naphthacene, naphthalene, pentacene, ovalene, 9,10-benzphenanthrene, 1,2-benzanthracene, 1,3,6,8-tetraphenylpyrene) into the corresponding perfluoroalicyclic compounds and of 1,4-dichlorobenzene into perfluorocyclohexane by 'LaMar' controlled-concentration direct-flow fluorination at room temperature and atmospheric pressure are now available in the patent literature,¹⁸ and precise details of the use of the method, in conjunction with a cryogenic reactor, to convert neopentane into perfluoroneopentane in low yield (10% after g.l.c. isolation) are also to hand.²¹ The results of kinetic studies on the direct fluorination of methane,²² [²H₂]methane,²³ halogenomethanes,²⁴ and olefins²⁵ are likewise in print. Treatment of the perfluoropropene dimers (CF₃)₂C:CF·CF₂·CF₃ and *trans*-(CF₃)₂CF·CF:-CF·CF₃ with fluorine at -78 °C yields perfluoro-(2-methylpentane) quantitatively, while fluorination of a mixture of the trimers [(CF₃)₂CF]₂C:CF·CF₃ and

²⁰ J. L. Margrave and R. J. Lagow, U.S.P. 3 758 450/1973 (*Chem. Abs.*, 1974, **80**, 60 546u); J. L. Margrave, R. B. Badachhape, A. P. Conray, J. J. Wang, and F. D. Catrett, *U.S. Nat. Tech. Inform. Serv., AD Reports*, 1972, No. 894 598/2GA (*Chem. Abs.*, 1974, **81**, 77 018s) (the direct fluorination of *o*-MeC₆H₄CO₂H, Ph₂O, MeCO₂Na, MeOCH₂·CO₂H, and natural rubber is also described).

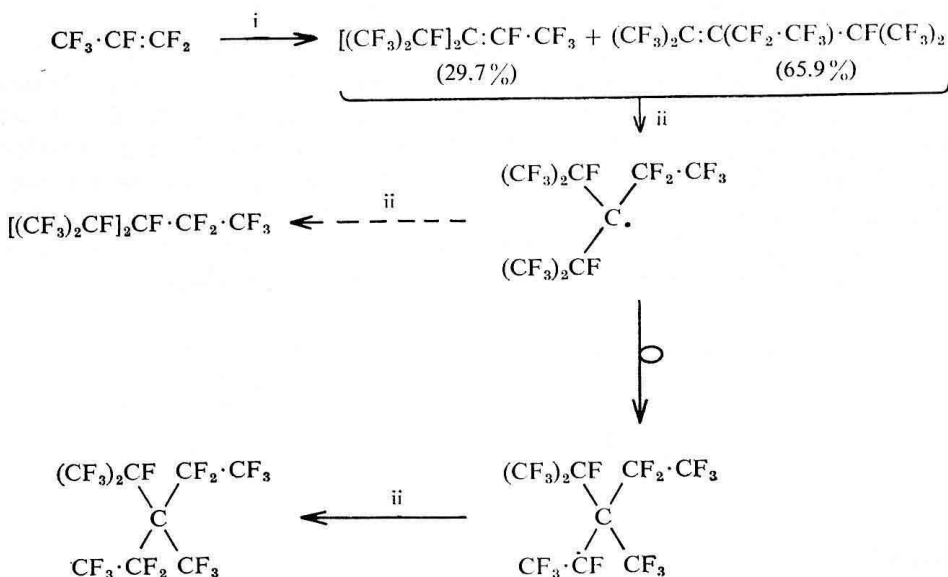
²¹ N. J. Maraschin and R. J. Lagow, *Inorg. Chem.*, 1973, **12**, 1458 (*cf.* the 'LaMar' low-temperature solid-substrate fluorination of hexamethylethane, *J. Amer. Chem. Soc.*, 1972, **94**, 8601).

²² N. G. Fedotov, V. I. Vedenev, and O. M. Sarkisov, *Doklady Akad. Nauk S.S.S.R.*, 1973, **208**, 401 (*Chem. Abs.*, 1973, **78**, 123 888p). For details of a novel nozzle reactor for the direct fluorination of methane see H. J. Diesner and K. Schugerl, *Adv. Chem. Ser.*, 1974, No. 133, p. 46 (*Chem. Abs.*, 1974, **81**, 169 023t).

²³ A. Persky, *J. Chem. Phys.*, 1974, **60**, 49.

²⁴ V. I. Vedenev, O. M. Sarkisov, M. A. Teitel'boim, and A. E. Shilov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1974, 1044; M. A. A. Clyne, D. J. McKenney, and R. F. Walker, *Canad. J. Chem.*, 1973, **51**, 3596 (mass spectrometric study of atomic F-H₂, F-Cl₂, F-CH₄, F-CHF₃, F-CH₃Cl, F-CH₂Cl₂, or F-CHCl₃ reactions); A. V. Pariiskaya, and V. I. Vedenev, *Kinetika i Kataliz*, 1973, **14**, 1116, 1365 (*Chem. Abs.*, 1974, **80**, 36 494e, 94 881q) (O₂ inhibition of CH₂F₂-F₂ and MeF-F₂ reactions).

²⁵ J. M. Parson, K. Shobatake, Y. T. Lee, and S. A. Rice, *J. Chem. Phys.*, 1973, **59**, 1402, 1416.



Reagents: i, $(\text{CF}_3 \cdot \text{CHF} \cdot \text{CF}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2)_3\text{N}$ [from $\text{CF}_3 \cdot \text{CF} : \text{CF}_2 + (\text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2)_3\text{N}$], Et_3N , MeCN , $45\text{--}50^\circ\text{C}$; ii, $\text{F} \cdot$ or F_2 .

Scheme 2

$(\text{CF}_3)_2\text{C} : \text{C}(\text{CF}_2 \cdot \text{CF}_3) \cdot \text{CF}(\text{CF}_3)_2$ provides the corresponding nonane $[(\text{CF}_3)_2\text{CF}]_2\text{CF} \cdot \text{CF}_2 \cdot \text{CF}_3$ ($\sim 95\%$) at 30°C but mainly its isomer $(\text{CF}_3)_2\text{CF} \cdot \text{C}(\text{CF}_3)(\text{CF}_2 \cdot \text{CF}_3)_2$ at 100°C , plausibly *via* the rearrangement depicted in Scheme 2.²⁶ Direct fluorination of the trimer $(\text{CF}_3)_2\text{CF} \cdot \text{CF} : \text{C}(\text{CF}_3) \cdot \text{CF}_2 \cdot \text{CF}_2 \cdot \text{CF}_3$ [from $\text{CF}_3 \cdot \text{CF} : \text{CF}_2 / (\text{CF}_3 \cdot \text{CHF} \cdot \text{CF}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2)_3\text{N} / \text{DABCO}$ in DMSO at $36\text{--}38^\circ\text{C}$] gives the perfluorononane $(\text{CF}_3)_2\text{CF} \cdot \text{CF}_2 \cdot \text{CF}(\text{CF}_3) \cdot \text{CF}_2 \cdot \text{CF}_2 \cdot \text{CF}_3$, while the tetramer $[(\text{CF}_3)_2\text{CF}]_2\text{C} : \text{C}(\text{CF}_3) \cdot \text{CF}(\text{CF}_3)_2$ [from oligomerization of $\text{CF}_3 \cdot \text{CF} : \text{CF}_2$ as in Scheme 2 but at higher temperatures], at 75°C (no reaction occurs at 20°C), undergoes cleavage with formation of $[(\text{CF}_3)_2\text{CF}]_2\text{CF} \cdot \text{CF}_2 \cdot \text{CF}_3$, $\text{CF}_3 \cdot \text{CF}_2 \cdot \text{CF}_2 \cdot \text{CF}(\text{CF}_3) \cdot \text{CF}(\text{CF}_3)_2$, and C_3F_8 .^{27,28} Treatment of *syn*-perfluoro-octamethyltricyclo-[4,2,0,0^{2,5}]octa-3,7-diene (from dimerization of perfluorotetramethylcyclobutadiene) or of its valence isomer perfluoro-octamethylcyclo-octatetraene (see p. 96) with fluorine at -78 to 100°C in an attempt to provide chemical evidence of structure (double bond 'count') gave complex mixtures which were not investigated.²⁹

Data provided by a kinetic study of the thermal ($280\text{--}450^\circ\text{C}$) fluorine-perfluoro-cyclobutane reaction [activation energy: $170 \pm 2 \text{ kJ mol}^{-1}$ ($40.5 \pm 0.5 \text{ kcal mol}^{-1}$); products: CF_4 , C_2F_6 , C_3F_8 , $n\text{-C}_4\text{F}_{10}$] have been discussed in terms of initiation by $S_{\text{H}}2$ attack of fluorine atom on ring carbon followed by the sequence presented in Scheme 3 (* indicates a thermally excited species).³⁰ The possibility that the $\text{C}_1\text{--C}_3$ fluorocarbons arose *via* fluorinolysis of perfluoro-*n*-butane formed first was excluded

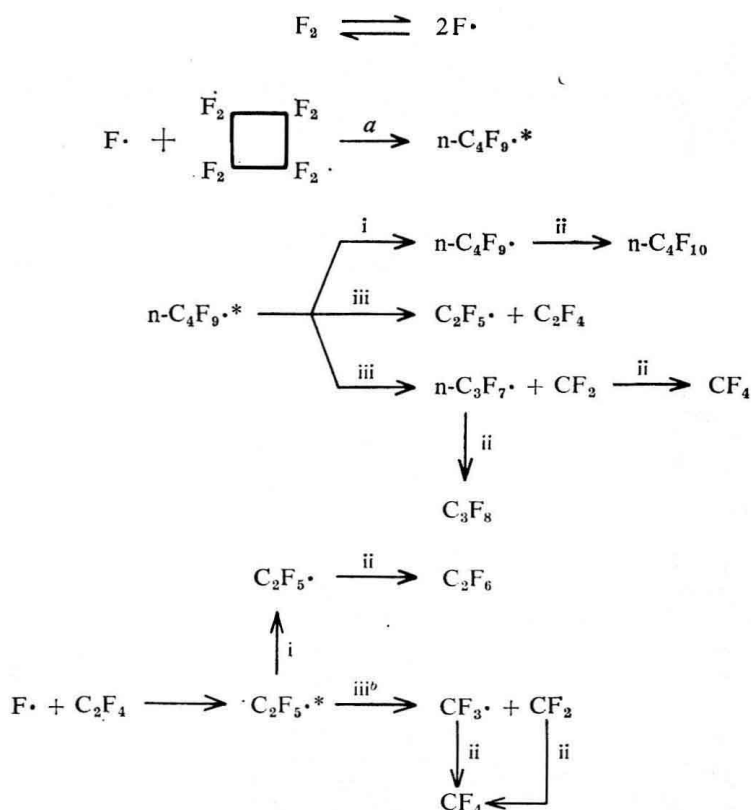
²⁶ S. P. von Halasz, F. Kluge, and T. Martini, *Chem. Ber.*, 1973, **106**, 2950 (see also p. 76).

²⁷ T. Martini and S. P. von Halasz, *Tetrahedron Letters*, 1974, 2129 (see also p. 76).

²⁸ For details of the anionic oligomerization of perfluoropropene, see p. 75).

²⁹ L. F. Pelosi, Ph.D. Thesis, Cornell University, 1973 [Univ. Microfilms, Ann Arbor, Mich., Order No. 73/22 517; see also *Diss. Abs. Internat. (B)*, 1973, **34**, 1428].

³⁰ J. B. Levy and R. C. Kennedy, *J. Amer. Chem. Soc.*, 1974, **96**, 4791.



Reagents: i, any molecule that can remove energy from the thermally excited radical by collision; ii, F_2 or $\text{F}\cdot$; iii, fragmentation.

Scheme 3

^a Exothermicity $-60 \text{ kcal mol}^{-1}$. ^b This step is necessary because the yield of CF_4 substantially exceeds that of C_3F_8 .

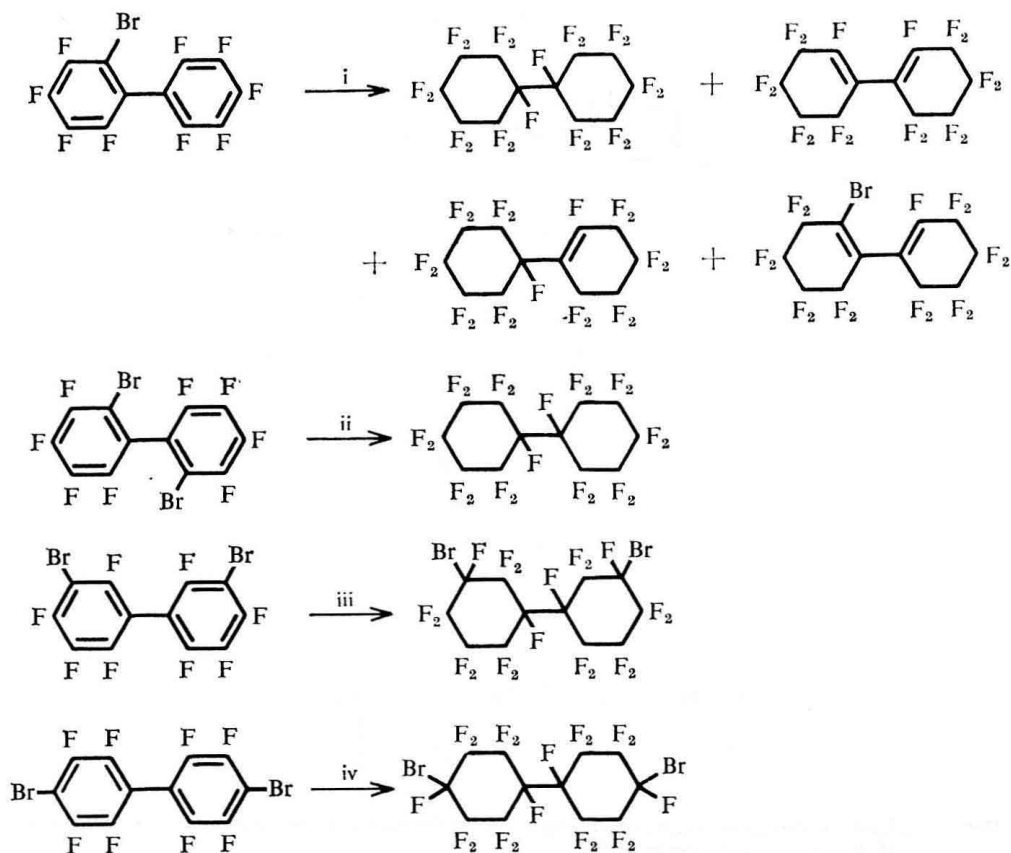
by lack of reaction in a separate experiment between perfluoropropane and fluorine at 477°C for 30 h, conditions under which perfluorocyclohexane likewise fails to suffer attack, the difference in reactivity between these fluorocarbons and perfluorocyclobutane presumably arising from ring-strain effects;³¹ consideration of fluorine atom displacement on the fluorine of a carbon-fluorine bond in such systems is unreasonable in view of the bond energies involved [$\text{F}-\text{F}$ 125 (37); av. $\text{C}-\text{F}$ 485 kJ mol^{-1} (116 kcal mol^{-1})].

Fluorinations of polyfluorobiphenyls with cobalt trifluoride (see Scheme 4),^{32a} hexafluorobenzene with cobalt trifluoride (\rightarrow cyclo- C_6F_{12} , cyclo- C_6F_{10} at $100-106^\circ\text{C}$; \rightarrow cyclo- C_6F_{10} , perfluorocyclohexa-1,4-diene at 50°C in the presence of CaCl_2),^{32b} polynuclear aromatics with potassium tetrafluorocobaltate(III) [e.g. (see also p. 57) pyrene \rightarrow perfluoroperhydropyrene at $360-410^\circ\text{C}$, decafluoro-

³¹ The authors of ref. 30 caution would-be investigators that mixtures of fluorine and fluorocarbons other than CF_4 are capable of thermal explosion.

^{32a} M. E. Harley and A. E. Pedler, *J. Fluorine Chem.*, 1973, 2, 399 [cf. $\text{C}_6\text{F}_5\text{Br} + \text{CoF}_3$ at 100°C \rightarrow mainly cyclo- $\text{C}_6\text{F}_{11}\text{Br}$ (J. Riera and R. Stephens, *Tetrahedron*, 1966, 22, 2555)].

^{32b} R. D. Chambers, D. T. Clark, T. F. Holmes, W. K. R. Musgrave, and I. Ritchie, *J.C.S. Perkin I*, 1974, 114.



Reagents: $\text{CoF}_3\text{-N}_2$ at i, 140°C (mass spectrometric evidence suggested that traces of perfluoro-2-bromobicyclohexyl were present in the mixture); ii, 250°C (at 140°C a complex inseparable mixture containing bromofluorocarbons was obtained); iii, 100°C ; iv, 140°C .

Scheme 4

biphenyl \rightarrow perfluorobicyclohexyl (ca. 64% yield) at 260°C ,^{32c} benzene with silver difluoride (\rightarrow cyclo- C_6F_{12} , cyclo- C_6F_{10} , and polyfluorocyclohexanes at $220\text{--}380^\circ\text{C}$),³³ potassium tetrafluoroargentate(III) (\rightarrow cyclo- C_6F_{12} , cyclo- C_6F_{10} , and polyfluorocyclohexanes at $180\text{--}380^\circ\text{C}$),³³ or potassium hexafluoronickelate(IV) (\rightarrow cyclo- C_6F_{12} , polyfluorocyclohexanes and -hexenes, 3,3,6,6-tetrafluorocyclohexa-1,4-diene, and fluorobenzenes at $100\text{--}250^\circ\text{C}$),³⁴ hexafluorobenzene, undecafluorocyclohexane, or decafluorocyclohexene with silver difluoride and with potassium tetrafluoroargentate(III) (\rightarrow cyclo- C_6F_{12} at 250°C),³³ and cyclohexanone or tetrahydrofuran with silver difluoride and with potassium tetrafluoroargentate(III)

^{32c} J. Burdon, J. R. Knights, I. W. Parsons, and J. C. Tatlow, *Tetrahedron*, 1974, 30, 3499.

³³ R. G. Plevy, M. P. Steward, and J. C. Tatlow, *J. Fluorine Chem.*, 1973/74, 3, 259. Both the AgF_2 and the KAgF_4 were prepared in the tubular reactors by passage of fluorine over Ag_2O and a 2:1 molar mixture of KCl and Ag_2O , respectively. For a review of previous work on AgF_2 as a fluorinating agent see M. Stacey and J. C. Tatlow, *Adv. Fluorine Chem.*, 1960, 1, 187.

³⁴ R. G. Plevy, R. W. Rendell, and M. P. Steward, *J. Fluorine Chem.*, 1973/74, 3, 267. The K_2NiF_6 was prepared by direct fluorination at 300°C of K_2NiCl_4 and of a 1:1 molar mixture of KCl and KNiF_3 .

(→ complex mixtures of fluorohydrocarbons) have been investigated using stirred-bed flow reactors. No problems were encountered in the use of silver difluoride despite the previous claim that a low-melting eutectic mixture of the difluoride and the monofluoride may be produced, although the tubular nickel reactor was attacked, resulting in contamination of the fluorinating agent with nickel difluoride. The new reagents $KAgF_4$ and K_2NiF_6 also behaved nicely as active components in the usual fluorine transfer-regeneration cycle, except that the former slowly became contaminated with the latter owing to attack on the nickel reactor. The products obtained by fluorination of benzene with the bright red hexafluoronickelate K_2NiF_6 (which becomes reduced to the yellow tetrafluoronickelate K_2NiF_4) do not differ significantly from those produced with cobalt trifluoride, but the former is the more vigorous reagent; the results of further work with this reagent³⁴ will be most welcome in view of the belief that complex nickel fluorides play a major role in Simons' electrochemical fluorination (see Vol. 2, p. 5).

Preliminary studies on the mechanism of electrochemical fluorination have been reported in the form of a note dealing with the voltammetric behaviour of arenes in anhydrous hydrogen fluoride,³⁵ and preparative Simons' electrochemical fluorination of benzene [→ CF_4 , CHF_3 , C_2F_6 , C_3F_8 , $n-C_4F_{10}$, $n-C_5F_{12}$, cyclo- C_6F_{12} (referred to below as C.P., common products), $n-C_6F_{14}$, cyclo- $C_5F_9 \cdot CF_3$], fluorobenzene (→ C.P., $n-C_6F_{14}$, cyclo- $C_5F_9 \cdot CF_3$), chlorobenzene (→ C.P., $n-C_6F_{14}$, CF_3Cl , cyclo- $C_5F_9 \cdot CF_3$, cyclo- $C_6F_{11}Cl$), *m*-dichlorobenzene (→ C.P., $n-C_6F_{14}$, CF_3Cl , cyclo- $C_6F_{11}Cl$, cyclo- $C_6F_{10}Cl_2$), anisole (→ C.P., $n-C_6F_{14}$, $n-C_6F_{13} \cdot OCF_3$, cyclo- $C_6F_{11} \cdot OCF_3$), *o*-chloroanisole (→ C.P., $n-C_6F_{14}$, CF_3Cl , $n-C_6F_{13} \cdot OCF_3$, cyclo- $C_6F_{11} \cdot OCF_3$, cyclo- $C_6F_{11}Cl$, cyclo- $C_6F_{10}Cl \cdot OCF_3$) (sodium fluoride was used as a conductivity aid in each of the foregoing cases), thiophenol (→ C.P., $n-C_6F_{14}$, cyclo- $C_5F_9 \cdot CF_3$, SF_6), *p*-chlorothiophenol (CF_4 , $n-C_5F_{12}$, cyclo- C_6F_{12} , $n-C_6F_{14}$, cyclo- $C_5F_9 \cdot CF_3$, cyclo- $C_6F_{11}Cl$, CF_3Cl , SF_6), *m*-thiocresol (→ C.P., cyclo- $C_6F_{11} \cdot CF_3$, SF_6), 2-chloropyridine [→ C.P. except cyclo- C_6F_{12} , perfluoro-(*N*-fluoropiperidine), $C_5F_{11}Cl$, CF_3Cl , NF_3], 3-chloropyridine [→ C.P. except cyclo- C_6F_{12} , cyclo- $C_5F_{10}NF$, $C_5F_{11}Cl$, perfluoro-(*N*-fluoro-3-chloropiperidine), NF_3],³⁶ branched perfluoroalkenes [*e.g.* $(CF_3)_2C:CF \cdot CF_2 \cdot CF_3 \rightarrow (CF_3)_2CF \cdot CF_2 \cdot CF_2 \cdot CF_3$ (78% yield)],³⁷ *gem*-difluorocycloalkanes [*e.g.* 1,1-difluorocyclohexane (in the presence of CoF_2 and NaF) → cyclo- C_6F_{12} , cyclo- $C_5F_9 \cdot CF_3$],³⁸ and (trifluoromethyl)benzenes [*e.g.* $4-ClC_6H_4 \cdot CF_3 \rightarrow$ cyclo- $C_6F_{11} \cdot CF_3$, cyclo- $C_5F_8(CF_3)_2$ -1,2, and perfluoro-(1-chloro-4-methylcyclohexane)]³⁹ has been described. Phillips direct electrofluorination (see Vol. 1, p. 14, and Vol. 2, pp. 11 and 21) has been used to prepare perfluoropropane from propane⁴⁰ and propyl chloride.⁴¹

³⁵ J. P. Masson, J. Devynck, and B. Tremillon, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1974, **54**, 232.

³⁶ Y. Inoue, S. Nagase, K. Kodaira, H. Baba, and T. Abe, *Bull. Chem. Soc. Japan*, 1973, **46**, 2204.

³⁷ S. Benninger, Ger. Offen. 2 302 132/1974 (*Chem. Abs.*, 1974, **81**, 151 510q).

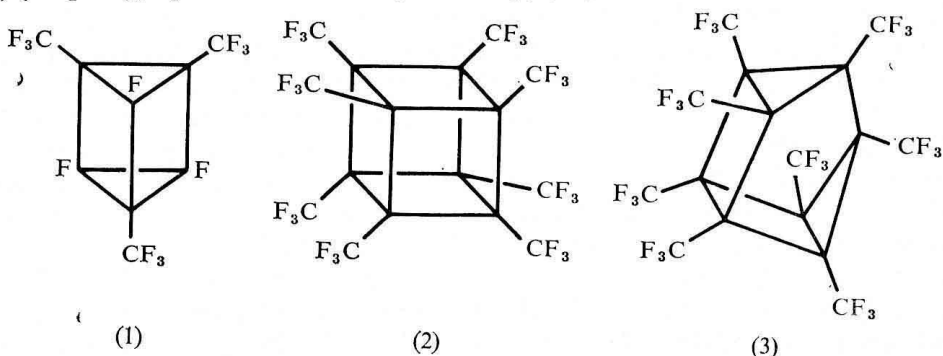
³⁸ D. Sato, K. Yamanouchi, and R. Murashima, Japan. Kokai 73 76 841 (*Chem. Abs.*, 1974, **80**, 82 239y).

³⁹ S. Nagase, H. Baba, K. Kodaira, T. Abe, and M. Yonekura, Ger. Offen. 2 313 863/1973 (*Chem. Abs.*, 1974, **80**, 70 429x).

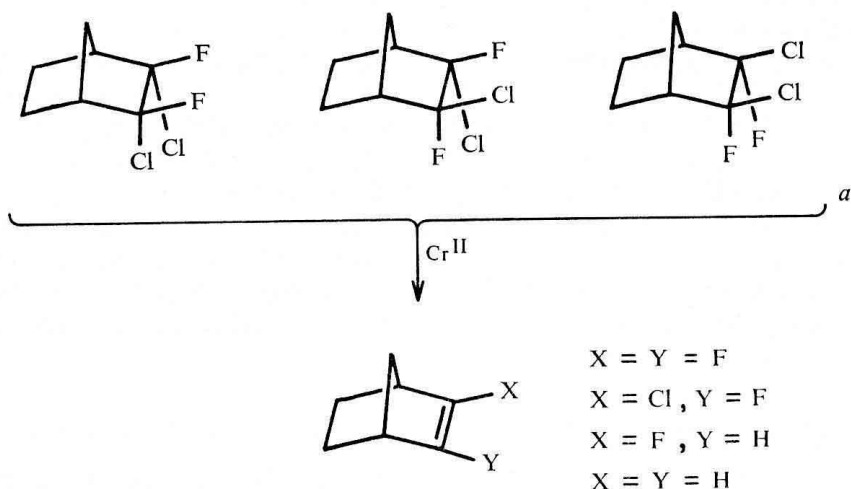
⁴⁰ R. A. Paul and M. B. Howard, U.S.P. 3 840 445/1974 (*Chem. Abs.*, 1975, **82**, 49 313m); see also K. L. Mills, U.S.P. 3 806 432/1974 (*Chem. Abs.*, 1974, **81**, 9182r).

⁴¹ H. M. Fox, U.S.P. 3 709 800/1973 (*Chem. Abs.*, 1973, **78**, 110 532t).

The cage compounds perfluoro-(1,3,5-trimethyltetracyclo[2,2,0,0^{2,6},0^{3,5}]hexane) (1) (see p. 92),⁴² perfluoro-octamethylcubane (2) (m.p. 253—254 °C), and perfluoro-



octamethylcuneane (3) (m.p. 186—187 °C) (see p. 96)²⁹ have been synthesized from unsaturated precursors. Defluorination of a commercial sample of perfluoro-(1,3,5-trimethylcyclohexane) with tri-iron tetraoxide at 475—490 °C was used to procure the perfluoro(trimethylbenzenes) (see p. 92) needed to prepare the prismane (1), which, despite its moderate thermal stability [half-life in solution towards reversion to perfluoro-(1,3,5- and 1,2,5-trimethylbicyclo[2,2,0]hexa-2,5-diene) (4 and 5), 19 h at 35 °C] has avoided isolation, owing, it appears, to catalysis of its isomerization to the Dewarbenzenes (4) and (5) by glass and other surfaces.⁴² Interestingly, defluorination of each of the thermal head-to-head dimers of $\alpha\beta\beta$ -trifluorostyrene (6) (see p. 86) to 3,3,4,4-tetrafluoro-1,2-diphenylcyclobutene (7) has been effected with chromous ion [$\text{Cr}_2(\text{SO}_4)_3$ -Zn dust- H_2O -DMF at 95 °C],⁴³ a reagent that was used previously by the same group⁴⁴ during work on the cycloaddition of *cis*- and



Scheme 5

^a Obtained by hydrogenation of the thermal 1,4-cycloadducts of *cis*/*trans*-CFCl:CFCl and cyclo- C_5H_6 .

⁴² M. G. Barlow, R. N. Haszeldine, and M. J. Kershaw, *J.C.S. Perkin I*, 1974, 1736.

⁴³ P. D. Bartlett and G. M. Cohen, *J. Amer. Chem. Soc.*, 1973, **95**, 7923.

⁴⁴ R. Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1970, **92**, 3822. Regarding the mechanism of the conversion of *vic*-dihalides (chlorides, bromides, and iodides) into alkenes by Cr^{II} , see D. M. Singleton and J. K. Kochi, *J. Amer. Chem. Soc.*, 1967, **89**, 6547.