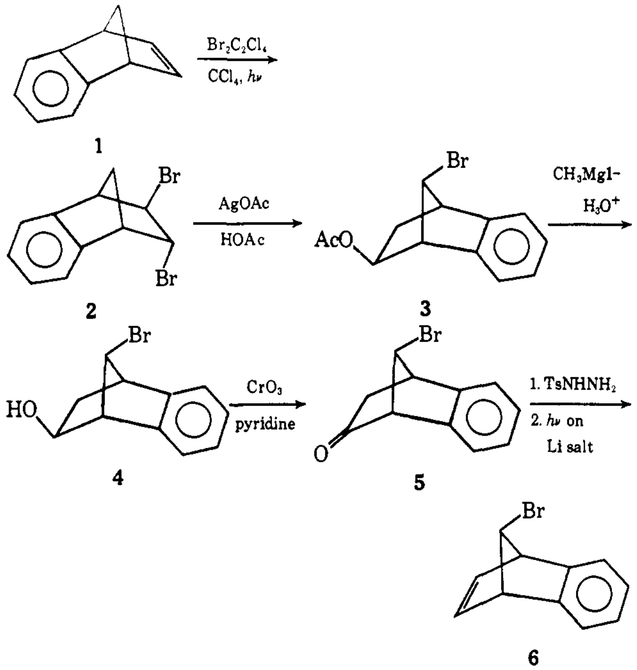
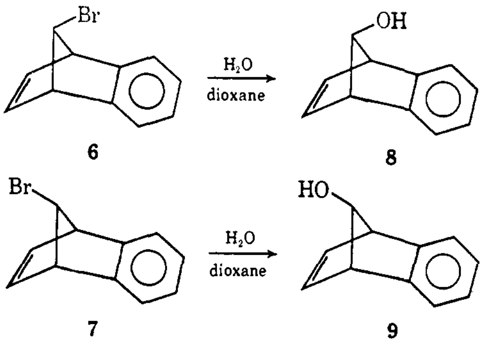
produced bromide **6** [mp 61.1–61.7°, λ^{KBr} 14.5 μ (HC=CH); $\delta^{\mathrm{CCl_4-CDCl_3}}$ 7.0–7.42 m (ArH, A_2B_2), 6.85 t (HC=CH), 4.64 t (–CHBr–), 3.99 q (bridgehead H's). *Anal.* Calcd for $C_{11}H_9Br$: C, 59.75; H, 4.10. Found: C, 59.87; H, 4.29].



The solvolysis of **6** in 80% ethanol was followed conductometrically: k_1 = (19.4°) 5.01×10^{-4} sec^{-1}; (25.4°) 1.09×10^{-3} sec^{-1}; (32.9°) 2.38×10^{-3} sec^{-1}; $\Delta H^{\ddagger} = 20.6$ kcal mol^{-1}; $\Delta S^{\ddagger} = -3.3$ eu. Bromide **6** is very reactive in solvolysis. Its rate at 25° is some 4.4×10^4 times faster than that of the *anti* epimer **7**[4] ($k_1 = 2.4 \times 10^{-8}$ sec^{-1} by Volhard titration) and nearly three times faster than that of *t*-butyl bromide ($k_1 = 3.85 \times 10^{-4}$ sec^{-1}).[5]

The solvolysis product from **6** in 70% dioxane containing 1.2 equiv of 2,6-lutidine was solely the *syn*-7-alcohol **8** (mp 92.5–94°). The alcohol and ether products in 80% ethanol were also only *syn*-7 derivatives.[6] Similarly, the *anti* epimer **7** afforded only the *anti*-7-alcohol **9**[7] in aqueous dioxane.



These results are of interest in the area of π participation and particularly in the contrast between aromatic and olefinic abilities to stabilize homoallylic cationic centers. It is curious that *both syn-* and *anti*-7-bromobenzonorbornadienes solvolyze with retention.

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[4] J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *J. Org. Chem.*, **32**, 893 (1967), report its synthesis. Its solvolysis was part of the present study.

[5] O. T. Benfey, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2494 (1952). We found a rate constant at 25.9° of 4.2×10^{-4} sec^{-1} by conductometry.

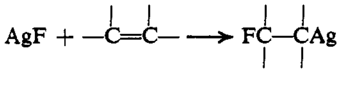
[6] All new compounds except **2** have been fully characterized by analysis and consonant spectra. Dibromide **2** had the proper spectra but was not as yet purified for analysis.

[7] P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

Perfluoroalkylsilver Compounds

Sir:

We wish to report the preparation of perfluoroalkylsilver compounds by the nucleophilic addition of silver fluoride to fluoro olefins.



$$AgF + -\overset{|}{C}=\overset{|}{C}- \longrightarrow F\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}Ag$$

The silver fluoride addition reaction has been investigated with perfluoropropene, 2-chloroperfluoropropene, and perfluoro-2-methyl-2-pentene. Unlike the previously known silver alkyls,[1] the perfluoro compounds are relatively stable materials which are soluble in organic solvents and can be isolated as solvates. They decompose thermally to yield perfluoroalkyl free-radical products and are useful as synthetic intermediates.

For example, 0.100 mol of AgF in 100 ml of CH_3CN absorbed 0.100 ± 0.005 mol of $CF_2{=}CFCF_3$, added as a gas during 2 hr at 25°, with solution of the AgF. Filtration of the brown reaction mixture under a nitrogen atmosphere yielded a clear light yellow solution of perfluoroisopropylsilver, $(CF_3)_2CFAg$, which slowly darkened on standing. The presence of the silver compound was shown by treating duplicates of the above filtered reaction product as follows. (1) The addition of HCl in CH_3CN at 0° yielded 0.095 mol of CF_3CHFCF_3 and AgCl. A reaction with water also yielded CF_3CHFCF_3. (2) The addition of bromine in CH_3CN at 0° gave 0.062 mol of $CF_3CBrFCF_3$ and AgBr. (3) Removal of CH_3CN to a final bath temperature of 60° (0.05 mm) left a residue corresponding in weight to $(CF_3)_2CFAg \cdot CH_3CN$. Heating the solvate at 100° during 1.5 hr gave as volatile products, in addition to CH_3CN, 0.007 mol of CF_3CHFCF_3, 0.002 mol of $CF_3CF{=}CF_2$, and 0.033 mol (66%) of $(CF_3)_2CFCF(CF_3)_2$. The residue contained 0.093 g-atom of Ag^0 and 0.002 g-atom of Ag^+. The reaction products CF_3CHFCF_3, $CF_3CF{=}CF_2$, and $CF_3CBrFCF_3$ were isolated by distillation and determined quantitatively by glpc with a 0.25 in. × 15 ft 20% dioctyl phthalate on Chromosorb P column at 25°. Their identities were confirmed by comparison of their infrared and mass spectra with those of authentic samples. The C_6F_{14} was separated by distillation. Its properties were bp 58.0° (745 mm); ir max (gas) 1290, 1272, 1248 (shoulder), 1151, 995, 982, 963, 894, 747, and 730 cm^{-1}; mass spectrum, molecular ion − 19, 319 ($C_6F_{13}^+$) (no molecular ion at 338); nmr (^{19}F) 56.6 and 144.3 ppm up-

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[1] Very few alkylsilver compounds are known. Methyl- and ethylsilver are sparingly soluble solids which decompose below room temperature: G. E. Coates and F. Glocking in "Organometallic Chemistry," H. Leiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 447.

field from $CFCl_3$ with an area ratio of 6:1 (lit. for $(CF_3)_2CFCF(CF_3)_2$: bp 58.5–59.0° (741 mm),[2] 60.0° (756 mm);[3a] ir max 1299, 1277, 1149, 1009, 980, 961, 892, 747, and 722 cm^{-1} [3b]).

Perfluoro-2-methyl-2-pentene, $CF_3CF_2CF{=}C(CF_3)_2$,[4] bp 50.5°, 0.040 mol, was added to 0.040 mol of AgF in 100 ml of CH_3CN during 1 hr with solution of the AgF to form perfluoro-1,1-dimethylbutylsilver, $CF_3CF_2CF_2C(CF_3)_2Ag$. The addition of HCl yielded 0.025 mol of $CF_3CF_2CF_2CH(CF_3)_2$, ir max (gas) 2985 (C–H), with strong absorption at 1358, 1288, 1240, 1210, and 1111 cm^{-1}, determined by glpc and isolated by drowning in water, followed by distillation and preparative glpc. The glpc retention times and infrared spectrum found for $CF_3CF_2CF_2CH(CF_3)_2$ were identical with those of an authentic sample.[5] A second preparation of $CF_3CF_2CF_2C(CF_3)_2Ag$ with 0.100-mol quantities yielded, after treatment of the filtered reaction product with bromine, 0.094 mol of AgBr and 0.060 mol of $CF_3CF_2CF_2CBr(CF_3)_2$: bp 97.5° (745 mm); mass spectrum (high resolution), molecular ion at 399.8970 ($C_6{}^{79}BrF_{13}$, 399.8954); nmr (^{19}F) 62.5, 77.8, 100.5, and 116.3 ppm upfield from CCl_3F with area ratios of 6:3:2:2; ir max (strong) 1342, 1245–1300 (complex), 1130, 964, 931, 825, 735, and 713 cm^{-1}.

The above perfluoroalkylsilver compounds can also be conveniently prepared in sealed-glass ampoules. Using this technique a slow partial reaction was observed between $CF_3CF{=}CFCF_3$ and AgF in CH_3CN; $CF_2{=}CClF$ and $CF_2{=}CCl_2$ also gave as yet uninvestigated products. On the other hand, 2-chloroperfluoropropene added AgF in CH_3CN more rapidly than $CF_3CF{=}CF_2$, a result consistent with the expected greater stabilization of an "anionic" transition state by α-Cl as compared with α-F.[6] Treatment of the filtered $(CF_3)_2CClAg$[7] solution with bromine in CH_3CN yielded 73% C_3BrClF_6, bp 50.2–51.0° (743 mm); mass spectrum (high resolution), molecular ion at 263.8775 ($C_3F_6{}^{35}Cl^{79}Br$, 263.8775); ir max (strong) 1275, 1251, 1240, 936, 882, 748, and 707 cm^{-1} (lit.[8] for $CF_3CBrClCF_3$: bp 51–52°). Thermal decomposition of $(CF_3)_2CClAg$ at 100° was shown to form $(CF_3)_2CClCCl(CF_3)_2$, mp 92.1–93.5° (lit.[2b] mp 91.5–93.0°). Solutions of perfluoroisopropylsilver were also prepared in "tetraglyme," dimethylformamide, and benzonitrile using sealed ampoules. It was found that benzene, ethyl ether, and tetrahydrofuran could be added in large amounts to $(CF_3)_2CFAg$ in acetonitrile solution without the formation of a precipitate.

The formulation of the perfluoro olefin–silver fluoride addition products as perfluoroalkylsilvers is supported by the experimental results cited above, by the electron-deficient character of the fluoro olefins, and by previous observations on their addition reactions with metal fluorides. Such addition reactions to form fluorocarbanions reversibly as reaction intermediates were first observed with potassium fluoride, *i.e.*, the formation of fluoroalkylpotassiums,[9] and the prediction of a considerable chemistry for such ionic intermediates has been substantiated.[10] The order of reactivity for perfluoro olefins with silver fluoride in acetonitrile appears to be the same as that found with cesium and potassium fluorides.[4b] In anhydrous hydrogen fluoride, a solvent in which fluoride ion is unreactive but in which silver ion is a highly effective π-bonding reagent,[11] silver fluoride reacts only slowly with perfluoropropene at 125°.[12]

By comparison with the corresponding perfluoroalkylcesiums the perfluoroalkylsilver compounds described above are stable and covalent.[13] They do not readily transfer $R_F{}^-$ groups to sp^2 carbon or revert to metal fluoride and olefin.[14] They decompose homolytically at convenient temperatures. We believe that our observations with the silver compounds point to the synthesis of other fluoro organometallic compounds by addition of metal fluorides to fluoro olefins and to a significant new free-radical chemistry for such systems.

Acknowledgment. This work was supported by a grant from the National Science Foundation for which grateful acknowledgment is made.

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(2) M. Prober, Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1946. Prepared by: (a) $(CH_3)_2C{=}C(CF_3)_2 + F_2 \rightarrow (CF_3)_2CFCF(CF_3)_2$; (b) $CF_3CCl{=}CF_2 + F_2 \rightarrow (CF_3)_2CClCCl(CF_3)_2$ (W. T. Miller, Jr., in "Preparation, Properties and Technology of Fluorine and Organic Fluoro Compounds," C. Slesser and S. R. Schram, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p 678).

(3) R. D. Chambers, W. K. R. Musgrave, and J. Savory: (a) *J. Chem. Soc.*, 3779 (1961); (b) *ibid.*, 1993 (1962).

(4) (a) W. J. Brehm, K. G. Bremer, H. S. Eleuterio, and R. W. Meschke, U. S. Patent 2918501 (1959); (b) M. J. Roura (Fraticelli), Ph.D. Thesis, Cornell University, Ithaca, N. Y., 1965.

(5) Prepared by A. B. Clayton by the reaction of KHF_2 with $CF_3CF_2CF{=}C(CF_3)_2$ in aqueous acetonitrile.

(6) J. Hine and P. B. Langford, *J. Am. Chem. Soc.*, 79, 5497 (1957); J. Hine and A. D. Ketley, *J. Org. Chem.*, 25, 606 (1960).

(7) The possible α elimination of AgCl from chloroperfluoroalkylsilvers with transfer of methylene units such as $(CF_3)_2C$ is being investigated.

(8) B. L. Dyatkin, A. A. Gevorkyan, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1873 (1965).

(9) W. T. Miller, Jr., and J. H. Fried, 132nd National Meeting of the American Chemical Society, New York, N. Y., Abstracts, 1957, p 29M; J. H. Fried and W. T. Miller, Jr., *J. Am. Chem. Soc.*, 81, 2078 (1959); W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *ibid.*, 82, 3091 (1960).

(10) For a recent review see: J. A. Young, *Fluorine Chem. Rev.*, 1, 359 (1967).

(11) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, 79, 2495 (1957).

(12) W. T. Miller, Jr., M. B. Freedman, J. H. Fried, and H. J. Koch, *ibid.*, 83, 4105 (1961).

(13) A range of properties can be anticipated for the R_FAg's. No "primary" perfluoro compounds of the type R_FCF_2Ag have been prepared.

(14) The dimers and trimers which are readily formed from $CF_3CF{=}CF_2$ with CsF in CH_3CN at 25° [4b] were not significant products in the above experiments with $CF_3CF{=}CF_2$.

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Matrix Infrared Spectrum and Bonding in the Lithium Superoxide Molecule, LiO_2

Sir:

There has been a great deal of recent research activity on free radicals of the formula XO_2 where X = F,[1] Cl,[2] and H.[3] The bonding in these species is characterized by the O–O stretching frequencies which shift from 1495 to 1441 to 1101 cm^{-1} in the above order. Spratley and Pimentel[4] have rationalized this trend by suggesting that the X atom is bonded to an oxygen π^*

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(1) P. N. Noble and G. C. Pimentel, *J. Chem. Phys.*, 44, 3641 (1966); R. D. Spratley, J. J. Turner, and G. C. Pimentel, *ibid.*, 44, 2063 (1966).

(2) A. Arkell and I. Schwager, *J. Am. Chem. Soc.*, 89, 5999 (1967).

(3) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 38, 2627 (1963).

(4) R. D. Spratley and G. C. Pimentel, *J. Am. Chem. Soc.*, 88, 2394 (1966).