expected fluorocarbon on treatment with base. A 0.657 g. (2.09 mmoles) sample of $C_2F_5Mn(CO)_5$ gave 6.9 cc. (S.T.P.) of a mixture of fluoroform and 1,1-difluoroethylene after being heated (100° for 48 hr.) with base. Base hydrolysis of n-C_3F_7-$Mn(CO)_5$ affords small quantities of pentafluoroethane and fluoroform.

The infrared spectrum of the compound C_2-$F_5Fe(CO)_4I$ (m.p. 105–106° (dec.)) shows carbonyl stretching bands (C_2Cl_4 solution) at 2110 (w), 2070 (s), and 2049 (s) cm.$^{-1}$, bands due to C–F stretches (CS_2 solution) at 1302 (s), 1186 (s), 1047 (m), and 1031 (m) cm.$^{-1}$, and a C–C stretching band at 907 (s) cm.$^{-1}$. The F^{19} n.m.r. spectrum[4] of n-$C_3F_7Fe(CO)_4I$ shows resonances at 78.2 c.p.s. (CF_3 group), 54.9 c.p.s. (α-CF_2 group) and 114.4 c.p.s. (β-CF_2 group). Reaction of perfluoroalkyl iodides with iron pentacarbonyl below 50° is remarkable when compared with other known reactions of perfluoroalkyl iodides, which are usually chemically inert, reacting only when activated by ultraviolet light or by heating to near 200°.[5]

As an alternative approach to obtaining perfluoroalkyliron compounds, the reaction between iron pentacarbonyl and tetrafluoroethylene was investigated, and found to give the novel heterocyclic compound I, a white, volatile, air-stable solid (m.p. 76.5–77°, dec. 193°).

I
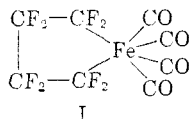
Anal. Calcd. for $C_8F_8O_4Fe$: C, 26.1; F, 41.3; Fe, 15.2; mol. wt., 368. Found: C, 26.0; F, 41.0; Fe, 15.2; mol. wt. (isopiestic), 367.

Treatment of I (0.832 g., 2.26 mmoles) with iodine (1.3 g., 5.1 mmoles) at 150° for 4 hr. gave 199 cc. (S.T.P.) of carbon monoxide (98.3% of theor.), demonstrating that I contains an Fe-$(CO)_4$ and not an $Fe(CO)_3$ group.[6] The F^{19} n.m.r. spectrum is entirely as expected for the proposed heterocyclic structure (I). Two resonances, barely resolvable as triplets, occur at 70.6 and 136.9 p.p.m.[4] In cyclic perfluoro-compounds, a CF_2 group not adjacent to a hetero-atom shows a resonance in the range 131.5–134.8 p.p.m.[7] The F^{19} resonance of a CF_2 group adjacent to a transition metal often occurs between 65–75 p.p.m.[4]

Compound I is extraordinarily stable for a substance in which a transition metal is bonded to an organo-group by σ-bonds. A sample of I failed to release carbon monoxide or fluorocarbon after being treated with bromine for 60 hr. at 50°. Further heating (70° for 120 hr.) afforded perfluorocyclobutane in 70% yield. When I is heated with triphenylphosphine no fluorocarbon is formed,

although triphenylphosphine invariably displaces organic moieties from π-hydrocarbon complexes of transition metals, a useful degradation reaction for characterization purposes.[8] Compound I appears to be stable indefinitely at room temperature, but a sample heated for 12 days at 160° formed perfluorocyclobutene quantitatively, probably *via* fluoride shift from CF_2 groups to iron, in a manner analogous to the decomposition of perfluoroalkyltin[3] and perfluorovinylboron[9] compounds. No tetrafluoroethylene has been detected as a product of any reaction of I.[6]

The least stable class of organo-compounds of transition metals is that in which metals are bonded to carbon by a simple σ-bond. The work described here shows that this type of bonding need not necessarily lead to instability. Perfluoroalkyl-iron compounds probably owe their high stability to the electronegativity of the perfluoro groups. The latter would remove electron density from transition metals far more efficiently than alkyl groups, and this removal of negative charge should lead to enhanced stability.[5]

(8) (a) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959); (b) R. B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. & Nucl. Chem.*, in press.

(9) S. L. Stafford and F. G. A. Stone, THIS JOURNAL, **82**, 6238(1960).

(10) National Science Foundation predoctoral fellow, 1958–61.

(11) Natvar Corporation Fellow at Harvard University, 1959–61.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY   T. A. MANUEL[10]
CAMBRIDGE 38   S. L. STAFFORD[11]
MASSACHUSETTS   F. G. A. STONE

A TRIFLUOROMETHYLBORON COMPOUND, CF_3BF_2[1]

Sir:

Tri-coördinate boron compounds having a B–CF_3 bond have been expected to be unstable for lack of any appreciable π-bonding from the CF_3 group to boron—such as is generally regarded as a stabilizing effect in BF_3 or even in $B(CH_3)_3$. The extreme case of $B(CF_3)_3$ has been discussed, with the conclusion that such a compound must easily lose CF_2 groups (as polymer) to form BF_3.[2] However, the existence of compounds of the CF_3BX_2 type (where X is an atom or group contributing π-bonding electrons to boron) was not precluded. Accordingly we now have made the enduringly metastable compound CF_3BF_2 by two very different methods at our respective institutions.

The Oregon State (OSC) method began with a reaction between $KB(n$-$C_4H_9)_2$[3] and CF_3I to form a white precipitate (KI) and a light-yellow ether solution presumably containing an etherate of

(4) F^{19} n.m.r. spectra of several perfluoroalkyl metal compounds have been studied by Miss E. Pitcher and will be reported later. Spectra were taken at 40 mc., and chemical shifts are given relative to CCl_3F as an internal standard.

(5) H. J. Emeléus, *Proc. Chem. Soc.*, 234 (1960); and references cited therein.

(6) Compound I appears to be identical with a material previously formulated as an olefin complex $(C_2F_4)_2Fe(CO)_3$ (K. F. Watterson and G. Wilkinson, *Chem. and Ind.*, 991 (1959)), to explain the existence of which a strange type of π-bonding had to be invoked.

(7) S. Brownstein, *Chem. Revs.*, **59**, 483 (1959).

(2) A. B. Burg, *et al.*, Eighth Annual Report to the Office of Naval Research, p. 25 (1954). The same question has been treated similarly by T. D. Parsons, ONR Technical Report No. 1, p. 2 (1958), and by J. J. Lagowski and P. G. Thompson, *Proc. Chem. Soc.*, 301 (1959).

(3) R. W. Auten and C. A. Kraus, THIS JOURNAL, **74**, 3398 (1952).

Bu_2BCF_3 or some more complex system containing B–CF_3 bonds. The filtered solution was evaporated, leaving a viscous, non-volatile liquid which would not react with $(CH_3)_3N$. However, it did react with BF_3 producing the volatile compounds $BuBF_2$ and CF_3BF_2. Alternatively, $KBBu_2$ could be made as a solution in $(C_2H_5)_3N$. Treatment with CF_3I, evaporation of the solvent and reaction of the product with dry HCl gave the presumed Bu_2BCF_3. This could be distilled under vacuum at room temperature (along with Bu_3B and other impurities) and again converted by BF_3 to CF_3BF_2 and $BuBF_2$. Evidence of the formula of CF_3BF_2 was the vapor-phase mol. wt. value 117.5 $\pm$ 1.5 (calcd. 117.8) and its formation of 1:1 adducts with $(CH_3)_3N$ and $(C_2H_5)_3N$, with recovery by action of dry HCl. Catalysts such as O_2 and glyptal resin caused its quantitative conversion to BF_3 and a white polymer, presumed to be $(CF_2)_n$. Fusion with potassium metal[4] and spectrophotometric analysis of the resultant soluble fluoride[5] gave 5.1F per CF_3BF_2.

The Southern California (USC) approach was based on the idea that a CF_3-S compound might attack a boron hydride to form H-S and B-CF_3 bonds. The disulfide CF_3SSCF_3[6] proved to be inert toward diborane, but could be used to make CF_3SCl,[7] and this reacted well enough with diborane during 15–18 hr. in sealed Pyrex containers at 60°. The ratio 2.1 CF_3SCl per B_2H_6 seemed optimal for the desired product, which was easily separable from the accompanying H_2, BF_3, B_2H_6 and non-volatile white solids but not from CF_3SH and CF_3SSCF_3. A 0.658 mmole fraction (6 mm. at −78°), having average mol. wt. 126.8, reacted with 0.446 mmole of $(CH_3)_2O$ to form a slightly volatile solid adduct, leaving 0.212 mmole of mixed CF_3SH and CF_3SSCF_3, average mol. wt. 144.4. Hence the boron compound had mol. wt. 118.4 (calcd. for CF_3BF_2, 117.8) and had formed a 1:1 etherate. Weighed etherate samples, hydrolyzed with NaOH, yielded neither Cl^- nor any sulfur compound; moreover, the recovered ether, the acid-liberated CO_2 and the titrated boric acid all corresponded to the formula $(CH_3)_2O\cdot CF_3BF_2$. However, the fluoride analysis (method successful for $Et_2O\cdot BF_3$) gave one-third to one-half of the expected 5F per mole. A complicated mass spectrum for the etherate included CF_3^+ (69, strong), possible BF (29 + 30), possible BF_2 (48 + 49) and CF_2 (50). The infrared spectrum of the ethe-

(4) P. J. Elving and W. B. Ligett, *Ind. Eng. Chem., Anal. Ed.,* **14,** 449 (1942).

(5) R. J. Bertolacini and J. E. Barney II, *Anal. Chem.,* **30,** 202 (1958).

(6) G. A. R. Brandt, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.,* 2198 (1952).

(7) The process CF_3SSCF_3 + 5.3NH_3 → H_2NSCF_3 + brown solids, occurring easily (or even explosively if not controlled) in liquid ammonia above −77°, was described by G. L. Juvinall, M.Sc. Thesis, USC Libraries, 1956, p. 9. The then-new compound H_2NSCF_3 was converted by HCl to CF_3SCl, as later reported by H. J. Emeléus and S. N. Nabi, *J. Chem. Soc.,* 1103 (1960); thus CF_3SCl was made more conveniently than by the earlier photochemical method of R. N. Haszeldine and J. M. Kidd, *ibid.,* 3219 (1953). Later $(CH_3)_3NH$ and CF_3SSCF_3 were used to make $(CH_3)_2NSCF_3$ for the same purpose. The vapor tensions of $(CH_3)_2NSCF_3$ (after reflux-fractionation at 0° to remove H-bonded amine, which persisted at lower temperatures) conformed to the equation log p_{mm} = 5.40514 − 0.004569T + 1.75 log T − 1783/T (78.25 mm. at 0°; b.p. 55.7°; Trouton constant, 21.4 cal./deg. mole).

rate (satd. vapor at 25°, meter-length cell) showed C–H stretching as a composite peak at 2800 cm.$^{-1}$, C–F stretching in the range 1160–80 and peaks at 1100 and 1115 possibly showing B–F stretching; other features were indistinct.

In the presence of mercury CF_3BF_2 slowly formed BF_3 and non-volatile white solids. An unstable anisole complex could be made, but diphenyl ether was inert. Trimethylamine displaced $(CH_3)_2O$ from the etherate, but BF_3 would not remove this ether, suggesting that CF_3BF_2 is a stronger Lewis acid than BF_3, as theory would demand.

DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE   THERAN D. PARSONS
CORVALLIS, OREGON   EVERETT D. BAKER
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA   ANTON B. BURG
LOS ANGELES 7, CALIFORNIA   GORDON L. JUVINALL
RECEIVED NOVEMBER 4, 1960

MECHANISM OF THE SERINI REACTION

Sir:

The Serini reaction[1] consists in refluxing a *vic*-diol monoacetate of type I with zinc dust in toluene and results in formation of the ketone III. The possibility that the reaction involves the 17,20-olefin was considered and experimentally eliminated by one of us and Huang-Minlon.[2] Shoppee's suggestion[3] that a 17,20-oxide is an intermediate was questioned by Wagle,[4] who found that under the conditions of the Serini reaction cholestane-$3\beta,5\alpha,6\beta$-triol 3,6-diacetate is converted to 3β-acetoxycholestane-6-one whereas the $3\beta,5\alpha,6\beta$-triol 3,6-diacetate is not. Wagle suggested a mechanism involving formation of the intermediate cyclic orthoacetate anion II and cleavage, with a 1,2-shift of hydrogen, to the ketone III and acetate ion.
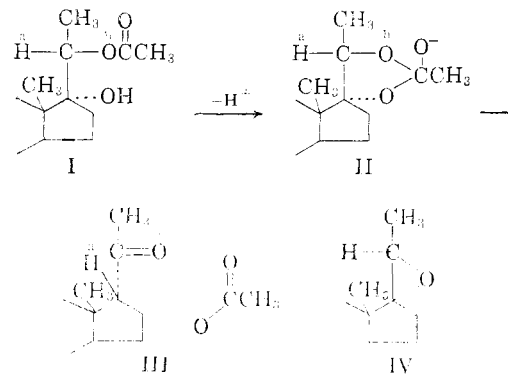
For clarification of the mechanism, we prepared these compounds and subjected each of them to the Serini reaction: 20β-deuterio-Δ^5-pregnene-$3\beta,17\alpha,$-20α-triol 3,20-diacetate (Ia), 20α-O^{18}-Δ^5-pregnene-$3\beta,17\alpha,20\alpha$-triol 3,20-diacetate (Ib), and 3β-α-(tetrahydropyranoxy)-$17\alpha,20$-oxido-Δ^5-pregnene (IV). The results all support the Wagle mechanism: 20β-H migrates to C_{17} with inversion at this site; C_{20}—O— changes to C_{20}=O; the 17,20-oxide IV does not function as an intermediate.

(1) A. Serini, W. Logemann and W. Hildebrand, *Ber.,* **72,** 391 (1939).

(2) L. F. Fieser and Huang-Minlon, *J. Am. Chem. Soc.,* **71,** 1840 (1949).

(3) C. W. Shoppee, *J. Chem. Soc.,* 1671 (1949).

(4) S. S. Wagle, Dissertation, Harvard University, 1949.