

A minor side-reaction observed is dissociation of the intermediate II to the thioamide derived from I and the nitrile (or presumably iminochloride when $R^1 \neq H$) derived from the initially-added thioamide.¹⁸ This side-reaction can be utilized to advantage in the synthesis of 2-unsubstituted 4-mercaptopyrimidines from *o*-aminonitriles and thioformanilide by employing dimethylformamide-hydrogen chloride as the reaction medium. The thioamide derived from I by the exchange reaction is formylated by the dimethylformamide-hydrogen chloride mixture (a variant of the Vilsmeier-Haack procedure) and the resulting *o*-formylaminothioamide then cyclizes under the reaction conditions to the same 4-mercaptopyrimidine obtained *via* the *m*-thiazine pathway pictured above. Improved yields are thus generally obtained.

(16) C. J. Cavallito, C. M. Martini and F. C. Nachod, *THIS JOURNAL*, **73**, 2544 (1951).

(17) M. R. Atkinson, G. Shaw, K. Schaffner and R. N. Warrener, *J. Chem. Soc.*, 3847 (1956).

(18) E. C. Taylor and J. A. Zoltewicz, *THIS JOURNAL*, **82**, 2656 (1960).

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RECEIVED OCTOBER 10, 1960

CATALYSIS OF THE DIELS-ALDER REACTION

Sir:

The recent report¹ that certain Diels-Alder reactions are accelerated by aluminum chloride prompts us to outline the results of our own investigations, which are the subject of a patent.² We found that in the presence of catalysts of the Friedel Crafts type, for example aluminum chloride, stannic chloride, boron trifluoride, ferric chloride, titanium tetrachloride, *etc.*, a number of Diels-Alder additions could be effected under much milder conditions than those required in the absence of such catalyst.

A good example of this catalytic effect was shown in the reaction of butadiene with methyl vinyl ketone to afford 4-acetylcyclohexene. This reaction was originally investigated by Petrov,³ who reported yields of 75-80% on heating the reactants at 140° in a sealed tube for 8-10 hours. We found that similar yields of the adduct could be obtained by adding methyl vinyl ketone at room temperature to an excess of butadiene in benzene (or similar solvent) in the presence of the above-mentioned catalysts. Less than one molar proportion of catalyst could be used; thus with 0.18 mol. equiv. of stannic chloride, a 73% yield of the adduct was obtained after reaction during 1 hour. In the absence of catalyst no adduct was formed under otherwise similar conditions.

The results of our investigations with a range of dienes and dienophiles may be summarized: Of the dienophiles which were studied in conjunction with butadiene, only acrolein, methyl vinyl ketone, and acrylic acid gave useful yields of the Diels-Alder

(1) P. Yates and P. Eaton, *THIS JOURNAL*, **82**, 4436 (1960).

(2) Sir Robert Robinson and G. I. Fray, British Patent 835,840 (1960).

(3) A. A. Petrov, *J. Gen. Chem. U.S.S.R.*, **11**, 309 (1941).

adducts under the above conditions. The general utility of the catalysts was obviously subjected to a further limitation by the readiness with which many dienes polymerize. In comparative experiments with methyl vinyl ketone and titanium tetrachloride, 2,3-dimethylbutadiene and cyclopentadiene yielded only polymer and dimer, respectively,⁴ whereas butadiene afforded 4-acetylcyclohexene in 63% yield, and anthracene⁵ gave a 46% yield of 9,10-(acetylethano)-9,10-dihydroanthracene,⁶ m.p. 151° (2,4-dinitrophenylhydrazones, m.p. 194-195°).

(4) With 2,3-dimethylbutadiene, the use of a milder catalyst, *viz.*, zinc chloride, enabled the adduct to be obtained in 16% yield.

(5) At 40-45°.

(6) Satisfactory analyses were obtained.

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RECEIVED NOVEMBER 9, 1960

CHEMISTRY OF THE METAL CARBONYLS. VII. PERFLUOROALKYL IRON COMPOUNDS¹

Sir:

A new class of transition metal compound is represented by perfluoroalkyl derivatives of iron. These perfluoroalkyl transition metal compounds have properties significantly different from those of perfluoroalkyl derivatives of main group metals, or alkyl compounds of transition metals.

Iron pentacarbonyl (29 g., 150 mmoles) and *n*-perfluoropropyl iodide (25 g., 85 mmoles) were heated under nitrogen at 45° for 21 hr. in benzene (50 ml.). The mixture then was cooled and evaporated to dryness. Sublimation (25° at 10⁻¹ mm.) of the solid residue onto a probe cooled to 0° gave 11.0 g. (28% yield) of red crystalline *n*-C₃F₇Fe(CO)₄I (m.p. 69-70° (dec.)), soluble in organic solvents. *Anal.* Calcd. for C₃F₇O₄IFe: C, 18.1; F, 28.7; I, 27.4; Fe, 12.1; mol. wt., 464. Found: C, 18.2; F, 28.5; I, 27.3; Fe, 12.5; mol. wt. (isopiestic), 480.

The perfluoropropyliron compound reacts with iodine at 150° with quantitative release of four moles of carbon monoxide per mole of complex. Perfluoropropyliron tetracarbonyl iodide, however, is not attacked by water or concentrated hydrochloric acid, and is much more stable than alkyl iron compounds such as C₅H₅Fe(CO)₂CH₃.²

Whereas perfluoroalkyl derivatives of main group metals react rapidly with base at moderate temperatures with quantitative release of their perfluoroalkyl groups as C_{*n*}F_{2*n*+1}H,³ perfluoroalkyl derivatives of transition metals studied are much less affected by base. A sample (0.722 g., 1.56 mmoles) of perfluoropropyliron tetracarbonyl iodide heated (100° for 65 hr.) with concentrated sodium hydroxide solution (2 ml.) gave carbon monoxide and only 14.7 cc. (S.T.P.) of heptafluoropropane (42% of theor.), identified by its infrared spectrum. Moreover, certain perfluoroalkyl transition metal compounds do not give the

(1) Previous article in this series, T. A. Manuel and F. G. A. Stone, *THIS JOURNAL*, **82**, 6240 (1960).

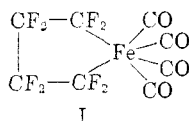
(2) T. S. Piper and G. Wilkinson, *J. Inorg. & Nuclear Chem.*, **3**, 104 (1956).

(3) H. C. Clark and C. J. Willis, *THIS JOURNAL*, **82**, 1888 (1960); H. D. Kaesz, J. R. Phillips, and F. G. A. Stone, *ibid.*, **82**, 6228 (1960).

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 $n-C_3F_7Mn(CO)_5$ affords small quantities of pentafluoroethane and fluoroform.

The infrared spectrum of the compound $C_2F_5Fe(CO)_4I$ (m.p. $105-106^\circ$ (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. spectrum⁴ of $n-C_3F_7Fe(CO)_4I$ shows resonances at 78.2 c.p.s. (CF_3 group), 54.9 c.p.s. ($\alpha-CF_2$ group) and 114.4 c.p.s. ($\beta-CF_2$ 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. $76.5-77^\circ$, dec. 193°).



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,

(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, 433 (1959).

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 perfluoroalkyltin³ and perfluorovinylboron⁹ 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).

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RECEIVED OCTOBER 12, 1960

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

(1) This joint contribution is based upon work supported by Office of Naval Research Contract Nonr-1286(04) at Oregon State College and N6onr-238(I) at the University of Southern California, where the work was supported also by the United States Air Force under Contract AF 33(616)-2743 monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. Reproduction is permitted for any purpose of the United States Government.

(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).