

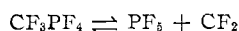
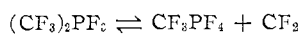
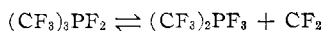
The Inorganic Chemistry of Carbon Difluoride

Sir:

The organic chemistry of divalent carbon has received much attention and has been proportionately rewarding. We now wish to describe some inorganic reactions of CF_2 at moderate temperatures; to this purpose we have prepared a new class of CF_2 transfer reagents, the trifluoromethyl fluorophosphoranes.

The new compound $(\text{CF}_3)_3\text{PF}_2$ (b.p. 20° , m.p. -102° , infrared absorption at 1240, 1195, and 855 cm^{-1}) is made by the action of SF_4 on $(\text{CF}_3)_3\text{P}^2$ at 25° . $(\text{CF}_3)_2\text{PF}_3$ (b.p. -5° , m.p. -74° , infrared absorption at 1240, 1195, 952, 890, and 790 cm^{-1}) can be made by SbF_3 fluorination of $(\text{CF}_3)_2\text{PCl}_3$,³ or more directly by the vigorous attack of SF_4 on $(\text{CF}_3)_2\text{PI}^2$ below room temperature. CF_3PF_4 (b.p. -35° , m.p. -117° , infrared absorption at 1240, 1190, 1018, 990, 915, and 900 cm^{-1}) is formed in the reaction of CF_3PCl_4 with SbF_3 .

The trifluoromethyl fluorophosphoranes are convenient sources of CF_2 . Elision of CF_2 occurs stepwise and reversibly



The reversibility is demonstrated by the reorganization of $(\text{CF}_3)_2\text{PF}_3$ (10% per day at 25°) to give $(\text{CF}_3)_3\text{PF}_2$ and CF_3PF_4 . CF_3PF_4 disproportionates (5% per month at 25°) to give $(\text{CF}_3)_3\text{PF}_2$, $(\text{CF}_3)_2\text{PF}_3$, and PF_5 , and the reaction of excess PF_5 with $(\text{CF}_3)_3\text{PF}_2$ (100° , 4 hr.) is a good synthesis method for CF_3PF_4 .

In the absence of other reagents the CF_2 disappears irreversibly by forming dimer (tetrafluoroethylene), trimer (hexafluorocyclopropane), and high polymer. Trimer is favored by slow decomposition ($(\text{CF}_3)_3\text{PF}_2$ at 120° for 24 hr. gave 10% $(\text{CF}_2)_2$, 80% $(\text{CF}_2)_3$, and 10% $(\text{CF}_2)_x$), while dimer is the major product when CF_2 is generated rapidly ($(\text{CF}_3)_3\text{PF}_2$ at 200° for 10 min. gave 80% $(\text{CF}_2)_2$, 10% $(\text{CF}_2)_3$, and 10% $(\text{CF}_2)_x$).

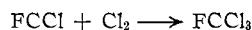
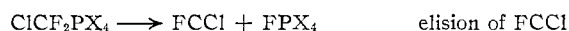
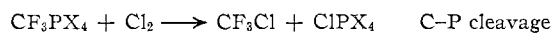
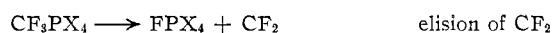
$(\text{CF}_3)_3\text{PF}_2$ decomposes at 25° in the gas phase at 0.5 atm. at the rate of 0.5% per month and at the same rate in the pure liquid. At 100° in the gas phase, CF_3 groups are destroyed to the same extent (40% in 17 hr.) in experiments with 4 and 0.25 atm. of starting material. This pressure and phase independence argues for a monomolecular elision process which suggests that the CF_2 is a true intermediate.

When $(\text{CF}_3)_3\text{PF}_2$ is decomposed in the presence of

other reagents (120° for 24 hr. are convenient conditions) the CF_2 may be intercepted. For example with iodine, CF_2I_2 is formed in 30% yield in addition to $\text{ICF}_2\text{CF}_2\text{I}$,⁵ $\text{ICF}_2\text{CF}_2\text{CF}_2\text{I}$,⁶ and $(\text{CF}_2)_3$. The new compound CF_2I_2 (*Anal. Calcd.*: I, 83.55; mol. wt., 304. Found: I, 83.40; mol. wt. (gas density), 298) is a yellow liquid: m.p. -72° ; 0° vapor tension 14 mm. the ultraviolet absorption maximum is at 2980 \AA . in the gas phase; infrared absorption of the gas is strong at 1120, 1070, and 745 cm^{-1} . F^{19} magnetic resonance shows a single line, 100 p.p.m. downfield from $\text{CF}_3\text{-COOH}$. CF_2I_2 reacts with mercury at room temperature to give tetrafluoroethylene.

CF_2 generated at 100° adds to HCl to give HCF_2Cl , which is of interest because it is probably the reverse of the reaction whereby C_2F_4 is formed from the pyrolysis of HCF_2Cl above 650° .⁷ CF_2 generated in the presence of oxygen gives carbonyl fluoride, but hydrogen does not react with CF_2 at 100° . CF_2 is a reducing agent in its reaction with UF_6 or MoF_6 , giving CF_4 and reduced metal fluorides.

The reaction with chlorine is complicated by a competing attack directly on $(\text{CF}_3)_3\text{PF}_2$. The products are CF_2Cl_2 (70%), CF_3Cl (20%), and CFCl_3 (10%). The elision of CF_2 accounts for the formation of CF_2Cl_2 and the direct cleavage of a C-P bond by chlorine gives rise to CF_3Cl . These events could account for the observed CFCl_3



No reaction with CF_2 was observed when $(\text{CF}_3)_3\text{PF}_2$ was pyrolyzed at 120° in the presence of BF_3 , CO , NF_3 , N_2O , PF_3 , CS_2 , SO_2 , or CF_3I . The CF_2 appeared as dimer, trimer, and high polymer and the reagents were recovered unchanged.

Our surmise that the CF_2 here described is a free molecule is supported by the constancy of reaction conditions for various reagents, the kinetics, and the nature of the products (especially CF_2I_2). We are seeking conclusive evidence by physical methods.

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