A-24

REACTION OF DIFLUOROCARBENE WITH COVALENT HALIDES

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In order to investigate the reaction of the halides MX_3 (M = P, As; X = F, Cl, Br, I), PCl_5, $POCl_3$, $POBr_3$, RSCl (R = Ph_3C, Ph, Et, Cl, SCl), $SOCl_2$, and WF_6 with CF_2 we used the complex $Cd(CF_3)_2 \cdot 2\ CH_3CN$ as precursor of CF_2. In accordance with Krause and Morrison [1] we found that this complex can also react as trifluoromethylation agent depending on the nature of the covalent halide and the reaction conditions. Already at room temperature $Cd(CF_3)_2 \cdot 2\ CH_3CN$ reacts with MX_3 (M = As; X = Cl, Br, I; M = P; X = Br, I), PCl_5, and S_2Cl_2 forming difluorohalomethyl compounds, e. g. X_2MCF_2X, by insertion of CF_2. The reaction products are thermically stable substances being rather resistant to hydrolysis in some cases. Only the iododerivatives decompose slowly to CI_2F_2 and to diphosphanes or diarsanes, resp.. In the reaction of CF_2 with oxohalides, however, COF_2 and the corresponding reduced halides are formed. On the other hand the cadmium complex reacts with RSCl (R = Cl, SCl, Et) as trifluoromethylation agent under substitution of chlorine by a CF_3-group forming trifluoromethylsulfanes and $CClF_3$.

1 L.J. Krause and J.A. Morrison: J. Am. Chem. Soc. 103 (1981) 2995.