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ADDITION OF SF_5Cl (AND TeF_5Cl) ACROSS C=C DOUBLE BONDS

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The SF_5-group is a substituent with a high (group)-electronegativity. Several methods are known to introduce this substituent into organic molecules, but only the addition of SF_5Cl is of preparative signification. The addition takes place with a radicalic mechanism. The direction to unsymmetrically substituted alkenes can be predicted by use of the anti-Markownikow-rules, if one assumes, that the SF_5-radical is added first. Tert-C-SF_5-compounds are not discribed in the literature, probably because tert-C-radicals are the most stable.

The reactivity of C-C multiple bonds is decreased by electron withdrawing substituents, especially by SF_5-groups. Therefore only traces of geminal substituted SF_5-compounds could be obtained by addition of SF_5Cl to vinyl-sulfurpentafluorides.

Now we found conditions to add SF_5Cl (and TeF_5Cl) to unreactive alkenes to obtain both a tert-C-SF_5-compound and a geminal SF_5-substituted alkene.

$$(F_3C)_2C{=}CH_2 + SF_5Cl \xrightarrow[\text{gas-phase}]{254\ nm} (CF_3)_2C(SF_5)CH_2Cl$$

$$F_2C{=}CHSF_5 + SF_5Cl \longrightarrow F_2ClC\text{-}CH(SF_5)_2$$

$$F_2C{=}CH_2 + TeF_5Cl \longrightarrow F_2ClC\text{-}CH_2\text{-}TeF_5$$

The analogous reaction with SeF_5Cl failed, the main products were SeF_4 and $ClH_2C\text{-}CF_3$.