Carbene C–H Insertion Reactions

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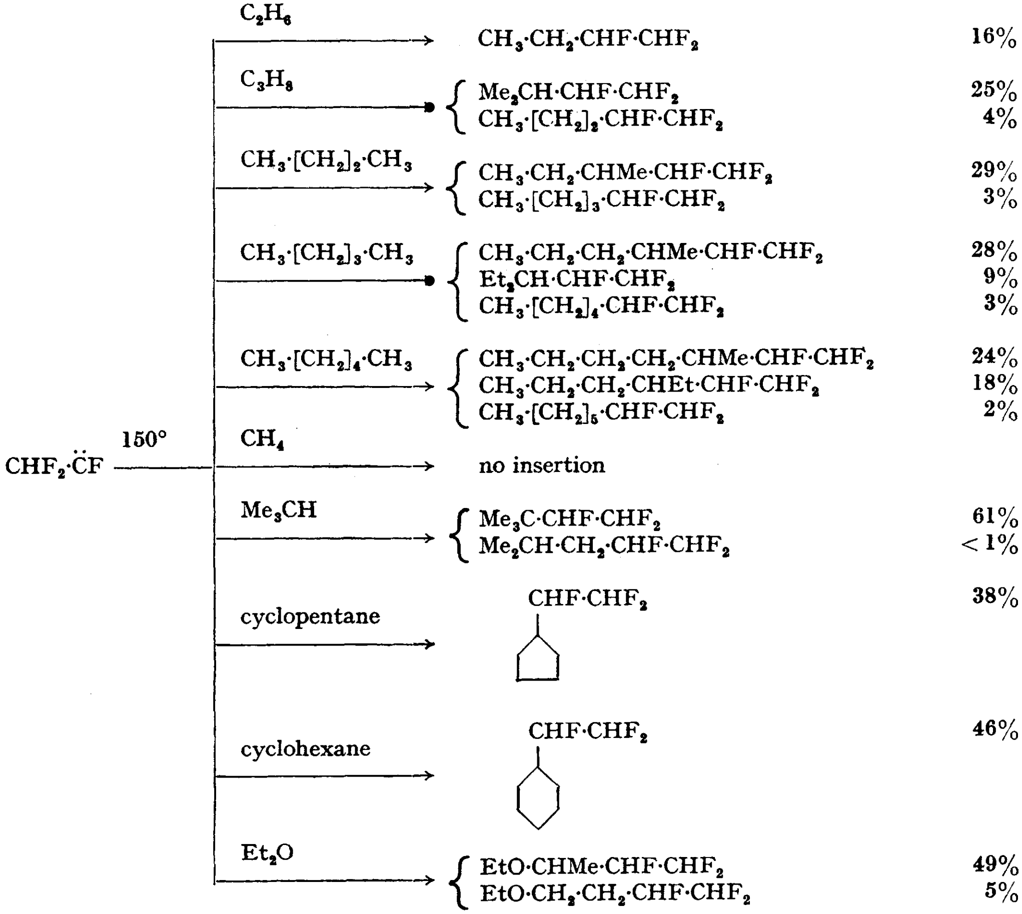
DIFLUOROMETHYLFLUOROCARBENE (1,2,2-trifluoroethylidene), readily prepared, in absence of a solvent and under neutral and mild conditions, by the general route to carbenes:[1]

$$SiHCl_3 + C_2F_4 \xrightarrow{\text{u.v.}} CHF_2{\cdot}CF_2{\cdot}SiCl_3 \xrightarrow{SbF_3}$$

$$CHF_2{\cdot}CF_2{\cdot}SiF_3 \xrightarrow{150^\circ} CHF_2{\cdot}\ddot{C}F_2{\cdot} + SiF_4$$

shows an appreciable degree of selective insertion into C–H bonds; its rearrangement to trifluoroethylene competes with, and sometimes predominates over, C–H insertion. Some typical reactions are as follows:

The products listed were separated by g.l.c. and identified by n.m.r. spectroscopy. The yields are based on the amount of difluoromethylfluorocarbene generated during the reaction and, since trifluoroethylene and the *cis–trans*-cyclopropanes, formed by reaction of trifluoroethylene with trifluoroethylidene, are the only other organic products, the yields indicate the relative ease of insertion into a C–H bond in different environments. No allowance has been made for the statistical availability of different types of hydrogen in the results summarized above. Precise kinetic studies are in hand. It is clear that carbene insertion into a secondary C–H is preferred to insertion into a primary C–H of an alkane. Thus,



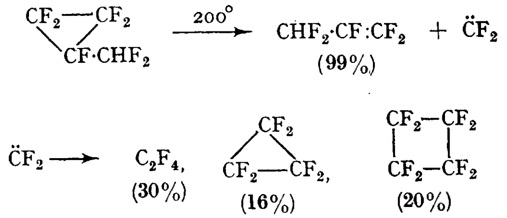
although insertion into a primary C–H occurs quite readily with ethane, attack on propane, n-butane, and the higher n-alkanes is almost entirely on the CH_2 groups. No attack at all could be detected on the CH_3 group of isobutane; the limit of g.l.c. detection was 1%. Attack on n-pentane or n-hexane shows that the CH_2 groups nearest the end of the chain are attacked rather more readily than those near the centre of the chain.

The tertiary hydrogen in isobutane is attacked exclusively and more easily than the C–H bonds in other hydrocarbons as shown by the decreased amount of trifluoroethylene formed. Methane was inert under the conditions used (100% trifluoroethylene formation).

Insertion reactions involving an ethylidene have not been reported previously; ethylidene itself, generated by photolysis or pyrolysis of diazoethane[2] or by photolysis of methylketene,[3] only undergoes rearrangement to ethylene in presence of hydrocarbons.

Difluoromethylfluorocarbene reacts with ethylene, tetramethylethylene, tetrafluoroethylene, or cyclohexene to give the corresponding cyclopropanes (75—90% yields); 100% stereospecific addition occurs with *cis*- or *trans*-but-2-ene (95% yields), implying the possibility of a singlet state carbene. The fluoro-ethylidene is captured by tristrifluoromethylphosphine to give the compound $(CF_3)_3P:CF{\cdot}CHF_2$.

Pyrolysis of the cyclopropane derived from tetrafluoroethylene leads to liberation of difluorocarbene in accord with other results reported recently:[4]



The greater stability of difluorocarbene compared with a fluoroethylidene is reflected by its reluctance to undergo C–H insertion reactions under conditions where difluoromethylfluorocarbene readily affords C–H insertion products. The fluoroethylidenes thus appear to have a blend of properties that make them uniquely suitable for the detailed study of C–H insertion reactions now in progress.

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