The Reaction of Hexafluoroacetone Azine with Olefins

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Summary The thermal reaction of hexafluoroacetone azine with electron-rich olefins yields either 1,1-bis(trifluoromethyl)cyclopropanes or criss-cross addition products.

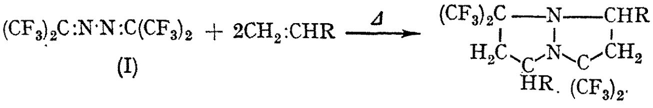
HEXAFLUOROACETONE AZINE[1] (I) has been reported[2] to react thermally with cyclohexane to give 2,2,2-trifluoro-1-(trifluoromethyl)ethylcyclohexane in a reaction analogous to a bis(trifluoromethyl)carbene insertion. We now report novel reactions of (I) with electron-rich olefins in which the type of product depends on the structure of the olefin. The thermal reaction (*ca.* 180°) of *cis*- or *trans*-but-2-ene with (I) gives a 1 : 4 mixture of *cis*- and *trans*-1,2-dimethyl-3,3-bis(trifluoromethyl)cyclopropane (32%). Reaction with cyclohexene gives 7,7-bis(trifluoromethyl)norcarane (21%) and 3-(2,2,2-trifluoro-1-trifluoromethylethyl)cyclohex-1-ene (8%). These products have been observed previously[3] from the reactions of bis(trifluoromethyl)diazirine with these olefins.

Azine (I) is stable to 240° and thus, under the conditions employed above, initial formation of bis(trifluoromethyl)-carbene followed by attack of this on the olefins is unlikely. At higher temperatures (570°) flow pyrolysis of (I) gives high yields of hexafluoroethane and trifluoroacetonitrile rather than products expected from the intermediacy of bis(trifluoromethyl)carbene.[4]

In contrast to the above results, thermal reaction of (I) with olefins of the type $CH_2:CHR$ (where R = H, Me, or Et) gives the "criss-cross" (1,3-:4,2-) addition products (II) (R = H, 58%; R = Me, 51%; R = Et, 78%).

The structures of the adducts (II) were established by elemental analysis, n.m.r. spectroscopy, mass spectrometry, and by pyrolysis which in all cases gave 1,1-bis(trifluoromethyl)ethylene. Pyrolysis thus shows the orientation of addition.

"Criss-cross" addition reactions between relatively electron-rich azines and electron-deficient olefins have been reported previously, (*e.g.* ref. 5). We observed no reaction between (I) and maleic anhydride.



$(CF_3)_2C:N\cdot N:C(CF_3)_2 + 2CH_2:CHR \xrightarrow{\Delta}$

(I)

(II)

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