

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 AZINE¹ (I) has been reported² 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 previously³ from the reactions of bis(trifluoromethyl)diazirine with these olefins.

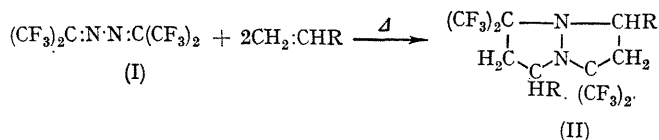
Azine (I) is stable to 240° and thus, under the conditions employed above, initial formation of bis(trifluoromethyl)carbene followed by attack of this on the olefins is unlikely. At higher temperatures (570°) flow pyrolysis of (I) gives high

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 $\text{CH}_2\text{:CHR}$ (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.



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² W. J. Middleton, D. M. Gale, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1968, **90**, 6813.

³ D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1966, **88**, 3617.

⁴ T. P. Forshaw and A. E. Tipping, unpublished results.

⁵ M. Haring and T. Wagner-Jauregg, *Helv. Chim. Acta*, 1957, **40**, 852; D. B. Dutt and P. C. Guha, *J. Indian Chem. Soc.*, 1950, **27**, 151.