

Preliminary Note

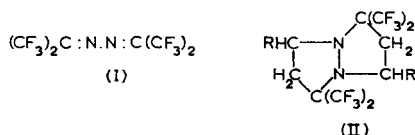
Novel 1:1 adducts from the reaction of hexafluoroacetone azine with various olefins and 1,3-dienes; Diels-Alder adducts as intermediates in the formation of criss-cross 2:1 adducts

STUART E. ARMSTRONG AND ANTHONY E. TIPPING

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD (Gt. Britain)

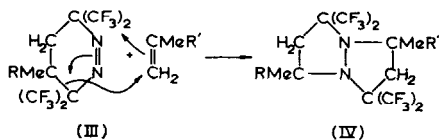
(Received September 25, 1972)

Hexafluoroacetone azine¹ (I) has been reported^{2,3} to react thermally (160–180°) with electron-rich olefins of type H₂C=CHR (R = H, Me, or Et) to give “criss-cross” (1,3-:4,2-) adducts (II). In contrast, *cis*- or *trans*-but-2-ene and cyclohexene react under comparable conditions to give nitrogen and products derived formally from addition and insertion reactions of bis(trifluoromethyl)carbene, although it is doubtful if the free carbene is involved^{2,4}. The reaction of azine (I) with alkanes is reported⁵ to involve a radical mechanism in which the diazo compound (CF₃)₂CN₂, and thence the carbene (CF₃)₂C:, is formed by a secondary process.



We now report further novel reactions of azine (I) with other electron-rich olefins and 1,3-dienes:

(a) Reaction of azine (I) with olefins of the type H₂C=CMeR at *ca.* 70° (12–24 h) gave high yields of Diels-Alder adducts (III) (R = Me, 91%; R = Et, 90%; R = Me₂CH, 96%). Further reaction of adduct (III) (R = Me) with an excess of isobutene (20°, 14 days) or of propene (0°, 14 days) afforded quantitative yields of the criss-cross adducts (IV) (R = R' = Me and R = Me, R' = H):

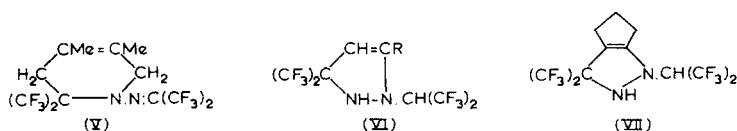


Similarly, 2,3-dimethylbuta-1,3-diene and azine (I) reacted at 40° (24 h) to give a mixture of the Diels-Alder adducts (III) (R = H₂C=CMe) (91%) and (V) (8%); the major adduct on reaction with propene (0°, 7 days) gave the 2:1

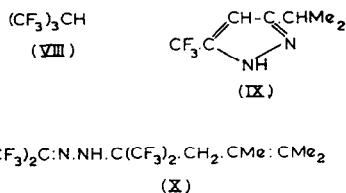
adduct (IV) ($R = H_2C=CMe$, $R' = H$) (100%). The 1:1 adducts (III) on flow pyrolysis ($350-400^\circ$, < 1 mmHg) undergo the retro-Diels-Alder reaction.

The comparable reactions of buta-1,3-diene, isoprene and cyclopentadiene at $20-40^\circ$, even in the presence of an excess of azine (I), gave only criss-cross adducts (90-98%); similarly, the olefins $H_2C=CHMe$ and $H_2C=CHEt$ when treated with excess azine (I) under mild conditions (20°) gave only criss-cross adducts (II).

(b) Reaction of azine (I) with olefins of the type $H_2C=CHR$ where R is a bulky group, *i.e.* Me_2CH or Me_3C , at *ca.* 100° or with cyclopentene at 140° gave Δ^3 -pyrazolines (VI) ($R = Me_2CH$, 85%; $R = Me_3C$, 96%) or (VII) (63%); with the olefin $H_2C=CH-CHMe_2$ the 2:1 adduct (II) ($R = CHMe_2$) (15%) was also formed and cyclopentene also gave nitrogen and a mixture (*ca.* 7%) of two $(CF_3)_2C$:olefin adducts.



Flow pyrolysis (450° , < 1 mmHg) of the pyrazoline (VI) ($R = Me_2CH$) gave the polyfluoroalkane (VIII) (100%) and the pyrazole (IX) (100%).



(c) Reaction of azine (I) with the olefin $H_2C=CMe-CHMe_2$ at 170° (45 h) gave nitrogen (51%), four $(CF_3)_2C$:olefin adducts (33%) and the 1:1 adduct (X) (15%) probably formed by an 'ene'-type reaction. The Diels-Alder adduct (III) ($R = Me_2CH$) formed by reaction at 70° was not detected and the recovered olefin fraction contained tetramethylethylene and reactant olefin in the ratio 4:1.

Tetramethylethylene did not react appreciably with azine (I) below 160° , but at 160° (24 h) the products were nitrogen, a mixture of $(CF_3)_2C$:olefin adducts (24%) and the 1:1 adduct (X) (43%); the recovered olefin fraction also contained tetramethylethylene and 2,3-dimethylbut-1-ene in the ratio 4:1. Trimethylethylene did not react with azine (I) appreciably below 170° and at 175° (20 h) nitrogen and a mixture (31%) of $(CF_3)_2C$:olefin adducts were obtained.

Pyrolysis of criss-cross adducts, Diels-Alder adducts and Δ^3 -pyrazolines has shown that these compounds are not precursors to the $(CF_3)_2C$:olefin adducts; it is also doubtful if 'ene'-type adducts are precursors since pyrolysis of adduct (X) resulted mainly in tar formation.

Thus at the present time there appear to be four distinct reaction paths by which azine (I) can react with an electron-rich olefin or 1,3-diene:

(i) Reaction to give criss-cross adducts *via* Diels–Alder adducts with olefins of type $\text{H}_2\text{C}=\text{CHR}$ ($\text{R} = \text{H}$ or straight chain alkyl) or $\text{H}_2\text{C}=\text{CMeR}$ ($\text{R} = \text{alkyl}$) or 1,3-dienes under relatively mild conditions. The intermediate Diels–Alder adducts are apparently isolable only with olefins or dienes which contain the $\text{H}_2\text{C}=\text{CMe}-$ grouping possibly because of steric hindrance to reaction of the 1:1 adduct with further olefin.

(ii) Reaction to give Δ^3 -pyrazolines with olefins of type $\text{H}_2\text{C}=\text{CHR}$ ($\text{R} = \text{branched chain alkyl}$) or cyclopentene at temperatures in the range $100\text{--}140^\circ$. The mechanism of this reaction is at present under investigation.

(iii) Reaction to give an ‘ene’-type 1:1 adduct which has only been observed in the reaction with 2,3-dimethylbut-1-ene at 170° .

(iv) Reaction to give $(\text{CF}_3)_2\text{C}:\text{olefin}$ 1:1 adducts with olefins of type $\text{RCH}=\text{CHR}$, $\text{R}_2\text{C}=\text{CHR}$ and $\text{R}_2\text{C}=\text{CR}_2$ and cyclohexene at *ca.* 160° ; isobutene also gives an adduct of this type (16%) when reacted at 160° ⁶.

All products gave satisfactory elemental analyses and spectral data.

REFERENCES

- 1 W. J. MIDDLETON AND C. G. KRESPAN, *J. Org. Chem.*, **30** (1965) 1398.
- 2 T. P. FORSHAW AND A. E. TIPPING, *Chem. Comm.*, (1969) 816.
- 3 T. P. FORSHAW AND A. E. TIPPING, *J. Chem. Soc. (C)*, (1971) 2404.
- 4 T. P. FORSHAW AND A. E. TIPPING, *J. Chem. Soc. Perkin Trans. I*, (1972) 1059.
- 5 W. J. MIDDLETON, *J. Amer. Chem. Soc.*, **93** (1971) 423.
- 6 S. E. ARMSTRONG AND A. E. TIPPING, unpublished results.