

Unsaturated Nitrogen Compounds containing Fluorine. Part IV.¹ Thermal Reactions of Hexafluoroacetone Azine with Hydrocarbon Terminal Olefins to give (1-Pyrazolin-1-yl)omethanides or Pyrazolines²

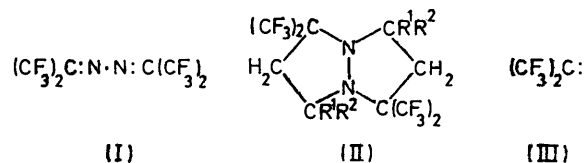
By **Stuart E. Armstrong** and **Anthony E. Tipping**,* Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Hexafluoroacetone azine reacts with olefins of the type $\text{CH}_2\text{:CMeR}$ ($\text{R} = \text{Me, Et, or Pr}^i$) at 60–70 °C to give the stable 1,3-dipolar azomethinimines [2-(1-pyrazolin-1-yl)propan-2-ides] $(\text{CF}_3)_2\text{C}^-\text{N}=\text{N}^+\text{C}(\text{CF}_3)_2\text{CH}_2\text{CMeR}$ in high yield (>90%), while with olefins of the type $\text{CH}_2\text{:CHR}$ ($\text{R} = \text{Pr}^i$ or Bu^t) the corresponding 3-pyrazolines $(\text{CF}_3)_2\text{CH}\text{N}\cdot\text{NH}\cdot\text{C}(\text{CF}_3)_2\text{CH}\text{:CR}$ are formed in high yield (>85%). Reaction of the azomethinimine ($\text{R} = \text{Pr}^i$) with isobutene at room temperature or with propene at 0 °C gives the corresponding criss-cross adducts (100%), but the pyrazoline ($\text{R} = \text{Pr}^i$) does not react with 3-methylbut-1-ene at 120 °C. Flow pyrolysis of the azomethinimines ($\text{R} = \text{Me}$ or Et) at 400 °C gives quantitative yields of the azine and the corresponding olefin, while flow pyrolysis of the pyrazoline ($\text{R} = \text{Pr}^i$) at 450 °C affords 1,1,1,3,3,3-hexafluoro-2-trifluoromethylpropane (100%) and the pyrazole $\text{Me}_2\text{CH}\cdot\text{C}\text{:N}\cdot\text{NH}\cdot\text{C}(\text{CF}_3)_2\text{CH}$ (100%).

HEXAFLUOROACETONE AZINE (I) reacts³ with hydrocarbon terminal olefins under thermal (160–180 °C) or photochemical conditions to give the corresponding criss-cross 2:1 adducts (II; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{H, Me, or Et}$) (>50%); electron-deficient olefins or acetylenes do not react under comparable conditions. In contrast reaction of the azine (I) with the non-terminal olefins, *cis*- or *trans*-but-2-ene or cyclohexene, gives products formally derived from the intermediacy of bis(trifluoromethyl)carbene (III).⁴

In the present work the thermal reactions of azine (I) with olefins of the type $\text{CH}_2\text{:CHR}$ ($\text{R} = \text{Et, Pr}^i$, or Bu^t) and $\text{CH}_2\text{:CMeR}$ ($\text{R} = \text{Me, Et, or Pr}^i$) have been investi-

gated. The conditions used and the products obtained are shown in the Table.



The reaction of azine (I) with isobutene at 160 °C gave only a low yield (17%) of the expected criss-cross adduct (II; $\text{R}^1 = \text{R}^2 = \text{Me}$) and substantial amounts of tar, nitrogen, 3,3,3-trifluoro-2-trifluoromethylprop-1-ene (IV),

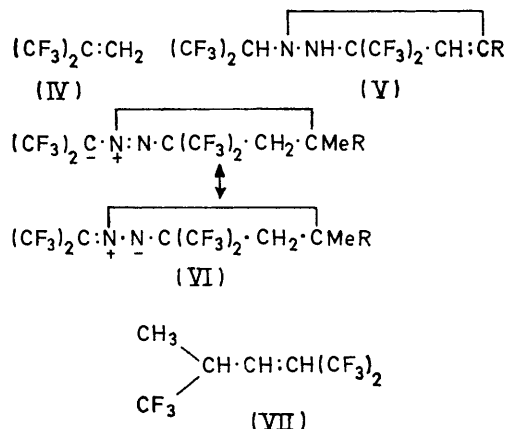
³ T. P. Forshaw and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 2404.

⁴ T. P. Forshaw and A. E. Tipping, *J.C.S. Perkin I*, 1972, 1059.

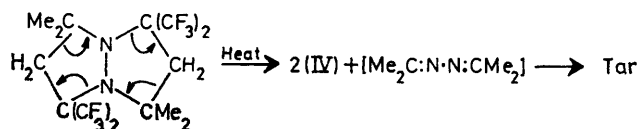
¹ Part III, S. E. Armstrong and A. E. Tipping, *J.C.S. Perkin I*, 1974, 2716.

² Preliminary communication, S. E. Armstrong and A. E. Tipping, *J. Fluorine Chem.*, 1973, **3**, 119.

1,1,1-trifluoro-4-methyl-2-trifluoromethylpent-2-ene (VII), and a multicomponent high-boiling liquid were also formed. Compound (IV) is formed in high yield (>80%) on pyrolysis (*ca.* 200 °C) of the criss-cross adducts (II; R¹ = H, R² = H, Me, or Et)³ and it is



considered that it arises similarly in the present case, *i.e.* by thermal decomposition of a proportion of the criss-cross adduct (II; R¹ = R² = Me) (Scheme 1). The



SCHEME 1

criss-cross adduct (II; R¹ = R² = Me) was therefore initially formed in at least 39% yield.

Reactions of hexafluoroacetone azine with hydrocarbon terminal olefins

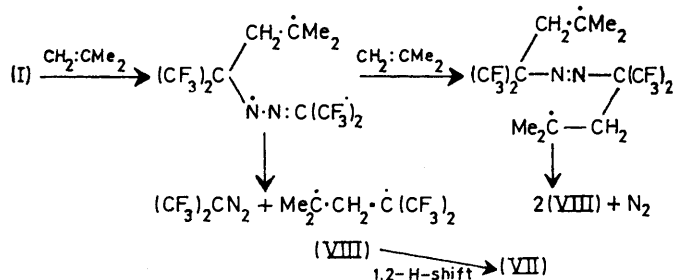
| Olefin CH ₂ :CR ¹ R ² | | Molar ratio olefin : azine | Temp. (°C) | Time (h) | Recovered reactants (%) | | Products (%) * | | | | | |
|--|-----------------|----------------------------|------------|----------|-------------------------|-------|----------------|--------------|-------|-----|-------|--------|
| R ¹ | R ² | | | | Olefin | Azine | N ₂ | (II) | (IV) | (V) | (VI) | Others |
| H | Me | 0.5 | 20 | 30 | | | 100 | | | | | |
| H | Me † | 2 | 170 | 24 | 14 | | 51 | <i>ca.</i> 4 | | | Tar | |
| H | Et | 0.5 | 20 | 30 | | | 100 | | | | | |
| H | Et | 0.33 | 60 | 24 | | | 100 | | | | | |
| H | Et † | 2 | 160 | 5 | 17 | 18 | 6 | 78 | Trace | | Tar | |
| H | Pr ¹ | 2 | 180 | 36 | 26 | | 9 | 15 | 4 | | Tar ‡ | |
| H | Pr ¹ | 3 | 100 | 15 | 62 | | | 15 | | | | |
| H | Bu ¹ | 0.5 | 110 | 24 | | 50 | | | | 85 | | |
| Me | Me | 2 | 160 | 36 | 13 | | 44 | 17 | 22 | 96 | Tar § | |
| Me | Me | 3 | 60 | 15 | 64 | | | 5 | | | 91 | |
| Me | Et | 1 | 70 | 24 | | | | | | | 90 ¶ | |
| Me | Pr ¹ | 1 | 70 | 12 | | | | | | | 96 | |

* Based on azine which had reacted. † Ref. 3. ‡ Minor multicomponent liquid (*ca.* 5%) also obtained. § The compound (CF₃)₂C:CH·CHMe₂ (VII) (16%) and a multicomponent liquid (*ca.* 15%) also formed. ¶ A four-component liquid (*ca.* 10%) was also obtained.

Olefin (VII) was identified by a comparison of its i.r. and n.m.r. spectra with those of the related compound (CF₃)₂C:CHMe.⁵ It is possibly formed as shown in Scheme 2. A similar diradical intermediate (XI) has been proposed previously⁴ to explain the formation of the *cis*- and *trans*-cyclopropanes (IX) and (X) in the ratio 1 : 4 from the thermal reactions of azine (I) with *cis*- or *trans*-but-2-ene. Pyrolysis of the *trans*-cyclopropane

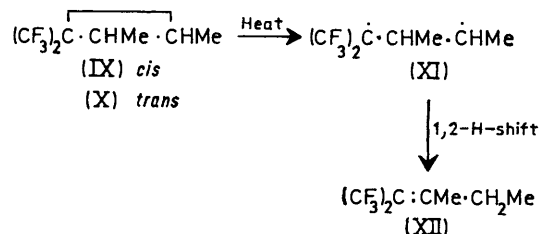
⁵ R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 1216.

(X) gave 1,1,1-trifluoro-3-methyl-2-trifluoromethylpent-2-ene (XII) (33%) as one of the products.⁴



SCHEME 2

The reason why diradical (XI) cyclises to the cyclopropanes (IX) and (X) while diradical (VIII) rearranges to olefin (VII) is probably the increased steric hindrance



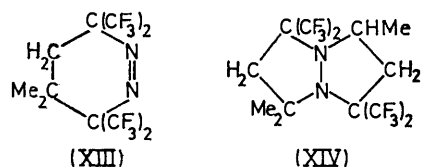
to cyclisation in (VIII). It is possible that the cyclopropane (CF₃)₂C·CH₂·CMe₂ is present as a minor product in the multicomponent mixture from which olefin (VII) was isolated by g.l.c.

In an attempt to minimise tar formation and increase the yield of the criss-cross adduct (II; R¹ = R² = Me)

the reaction of azine (I) with isobutene was investigated at a lower temperature (60 °C). At this temperature the major product was a 1 : 1 adduct (91%) and the criss-cross adduct was formed in low yield (5%) only. In the preliminary communication² the product was assigned the Diels–Alder adduct structure (XIII), but from a more recent investigation⁶ including X-ray analysis

⁶ K. Burger, W. Thenn, and A. Gieren, *Angew. Chem.*, 1974, **86**, 481; A. Gieren, P. Narayanan, K. Burger, and W. Thenn, *ibid.*, p. 482; K. Burger, W. Thenn, H. Schickaneder, and H. Peuker, *ibid.*, p. 483.

evidence has been obtained that the product is the azomethinimine (pyrazolinyliopropanide) (VI; R = Me); we agree with this latter assignment. The analogous reactions of the azine (I) with the olefins $\text{CH}_2\text{:CMeEt}$ and $\text{CH}_2\text{:CMe}\cdot\text{CHMe}_2$ also gave high yields ($\geq 90\%$) of the corresponding azomethinimines (VI; R = Et or Prⁱ) and the criss-cross adducts (II; R¹ = Me, R² = Et or Prⁱ) were not detected. It has also been observed² that 2,3-dimethylbuta-1,3-diene forms an analogous 1:1 adduct on reaction with the azine (I).



It was further shown that the azomethinimines (VI) are the precursors to the criss-cross adducts (II) by the reactions of the 1:1 adduct (VI; R = Me) with isobutene and propene. The reaction with isobutene was relatively slow at room temperature and gave the criss-cross adduct (II; R¹ = R² = Me) (100%), while the reaction with propene was much faster at 0 °C and yielded the criss-cross adduct (XIV) (100%).

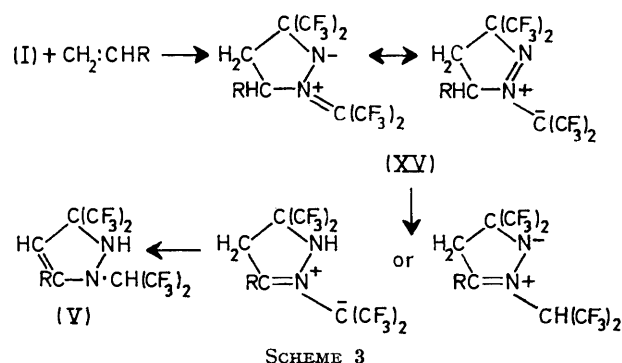
It was postulated by Huisgen⁷ that formation of criss-cross adducts between electron-rich azines and electron-deficient olefins proceeded *via* 1,3-dipolar (azomethinimine) intermediates. The adducts (VI) are the first examples of such azomethinimine intermediates to be isolated, thus proving that criss-cross adducts are indeed formed by 1,3-dipolar addition.

The azomethinimines (VI; R = Me or Et) when flow pyrolysed at 400 °C and low pressure (1 mmHg) gave quantitative yields of the azine (I) and isobutene or 2-methylbut-1-ene, *i.e.* the reverse reaction to their method of formation.

It was reported previously³ that azine (I) when treated with propene or but-1-ene at 160–170 °C gave the corresponding criss-cross adducts (II; R¹ = H, R² = Me or Et) (*ca.* 50%), together with nitrogen and tar. In the present work these reactions were reinvestigated at lower temperatures (propene at 20, but-1-ene at 60 and 20 °C) with an excess of azine (I) in an attempt to isolate the suspected azomethinimine intermediates. However, all the reactions gave quantitative yields of criss-cross adducts, and 1:1 adducts were not detected. The reactions of azine (I) with olefins of the type $\text{CH}_2\text{:CHR}$ were then extended to those containing more bulky alkyl groups (Prⁱ and Bu^t). At 180 °C the reaction with 3-methylbut-1-ene gave the criss-cross adduct (II; R¹ = H, R² = Prⁱ) (15%), together with tar and small amounts of nitrogen and olefin (IV), while at 100 °C the exclusive products were the criss-cross adduct (15%) and the 3-pyrazoline (V; R = Prⁱ) (85%). An analogous reaction with 3,3-dimethylbut-1-ene at 110 °C gave the 3-pyrazoline (V; R = Bu^t) (96%), and the criss-cross adduct (II; R¹ = H, R² = Bu^t) was not detected. It is possible that the 3-pyrazolines (V; R = Prⁱ or Bu^t) are formed

by rearrangement of the intermediate azomethinimines (XV; R = Prⁱ or Bu^t) (Scheme 3). However, it is surprising that the 3-pyrazolines (V; R = Me or Et) were not detected from the reactions of propene or but-1-ene with an excess of azine (I) at room temperature, conditions under which rearrangement of the azomethinimine intermediates (XV; R = Me or Et) would be expected at least to compete with further reaction with olefin to give the criss-cross adducts.

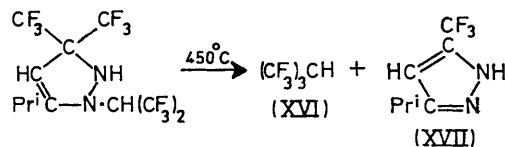
One explanation for these observations is that a bulky R group (Prⁱ or Bu^t) in the azomethinimine (XV) sterically hinders reaction with further olefin thus allowing rearrangement to the 3-pyrazolines (V) to compete successfully with criss-cross adduct formation. With less bulky R groups (Me or Et) in the azomethinimine (XV), criss-cross adduct formation is favoured over rearrangement. Alternatively the 3-pyrazolines (V) are formed by a route which does not involve 1,3-dipolar intermediates and in this respect it is interesting to note that reactions which gave azomethinimines (VI) and/or criss-cross adducts (II)



could be carried out at lower temperature (< 70 °C) than those which gave 3-pyrazolines (V) (100–110 °C).

The azomethinimines of type (VI) cannot rearrange to 3-pyrazolines because they do not possess hydrogen atoms on both carbons of the olefin residue.

The 3-pyrazolines are not also precursors to the criss-cross adducts (II) since attempted reaction of adduct (V; R = Prⁱ) with 3-methylbut-1-ene at 120 °C gave only unchanged reactants (100% recovered). On flow pyrolysis at 450 °C, however, adduct (V; R = Prⁱ) gave 1,1,1,3,3,3-hexafluoro-2-trifluoromethylpropane (XVI) (100%) and 3-isopropyl-5-trifluoromethylpyrazole (XVII) (100%). This unusual elimination of the type $\sigma 2_s + \sigma 2_s + \pi 2_s$, probably takes place by a thermally-allowed concerted mechanism.



EXPERIMENTAL

Techniques used were as described previously.¹ The g.l.c. columns employed are described in the text and the

⁷ R. Huisgen, *Angew. Chem.*, 1963, **75**, 604.

n.m.r. spectra were run using external trifluoroacetic acid and internal tetramethylsilane as the ^{19}F and ^1H references, respectively, unless stated otherwise. N.m.r. and mass spectral data for compounds marked with an asterisk are available in Supplementary Publication No. SUP 21222 (3 pp.).†

Hexafluoroacetone azine was prepared by treatment of the corresponding imine with potassium fluoride and bromine⁸ followed by photolysis of the resultant *N*-bromimine.⁹ The alkenes were commercial samples which, where necessary, were purified before use.

Reactions of Hexafluoroacetone Azine (I) with Olefins.—(a) *With isobutene at 160 °C.* A mixture of the azine (4.92 g, 15.0 mmol) and isobutene (1.68 g, 30.0 mmol), heated at 160 °C (36 h), gave (i) nitrogen (0.18 g, 6.57 mmol, 44%), (ii) a mixture (1.42 g, 10.60 mmol), which was shown by i.r. spectroscopy and g.l.c. (4 m Kel-F 10 oil at 28 °C) to consist of unchanged isobutene (0.22 g, 3.90 mmol, 13% recovered) and 3,3,3-trifluoro-2-trifluoromethylprop-1-ene (IV) (1.10 g, 6.70 mmol, 22%) (Found: M^+ , 164. Calc. for $\text{C}_3\text{H}_5\text{F}_6$: M , 164), (iii) a mixture (1.4 g) which was shown by g.l.c. (7 m TXP. at 100 °C) to contain four components in the ratio 18 : 2 : 3 : 3 and from which the major product was separated (g.l.c. as above) and identified as 1,1,1-trifluoro-4-methyl-2-trifluoromethylpent-2-ene (VII) * (0.97 g, 47.0 mmol, 16%) (Found: C, 40.8; H, 4.1%; M , 207. $\text{C}_7\text{H}_8\text{F}_6$ requires C, 40.8; H, 3.9%; M , 206), b.p. (Siwoloboff) 82 °C; λ_{max} 5.94s (>C=C< str.) μm , (iv) a higher-boiling mixture (0.6 g) containing ca. fifteen components (g.l.c., 2 m Apiezon L at 110 °C), and (v) a residue which was extracted from the reaction tube with carbon tetrachloride, the solvent was removed, and the resultant material sublimed *in vacuo* to give a residue of brown tar (1.95 g) and a white sublimate (1.15 g). The sublimate was recrystallised from carbon tetrachloride to give 2,2,6,6-tetramethyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (II; $\text{R}^1 = \text{R}^2 = \text{Me}$) * (1.10 g, 2.50 mmol, 17%) (Found: C, 38.0; H, 3.7; N, 6.4%; M^+ , 440. $\text{C}_{14}\text{H}_{16}\text{F}_{12}\text{N}_2$ requires C, 38.2; H, 3.6; N, 6.4%; M , 440), m.p. 92.5–93.5 °C.

(b) *With isobutene at 60 °C.* A mixture of the azine (1.64 g, 5.0 mmol) and isobutene (0.84 g, 15.0 mmol), sealed *in vacuo* in a Pyrex tube (ca. 100 cm³) and heated at 60 °C (15 h), gave unchanged isobutene (0.54 g, 9.67 mmol, 64% recovered) and a residue (1.94 g), which was extracted from the reaction tube with carbon tetrachloride and recrystallised from light petroleum (b.p. 40–60 °C) to give a solid (1.85 g) shown by g.l.c. (2 m Apiezon L at 110 °C) to consist of two components in the ratio 16 : 1. The mixture was separated by sublimation to give a residue of the 1,5-diazabicyclo[3.3.0]octane (II; $\text{R}^1 = \text{R}^2 = \text{Me}$) (0.11 g, 0.25 mmol, 5%) and a white sublimate of 2-(5,5-dimethyl-3,3-bis(trifluoromethyl)-1-pyrazolin-1-ylidene)-1,1,1,3,3,3-hexafluoropropan-2-ide (VI; $\text{R} = \text{Me}$) * (1.74 g, 4.54 mmol, 91%) (Found: C, 31.6; H, 2.2; N, 7.5%; M^+ , 384. $\text{C}_{10}\text{H}_8\text{F}_{12}\text{N}_2$ requires C, 31.3; H, 2.1; N, 7.3%; M , 384), m.p. 77–78 °C; λ_{max} 6.62s ($-\text{N}=\text{N}-$ str.) μm .

(c) *With 2-methylbut-1-ene.* A mixture of the azine (1.64 g, 5.0 mmol) and the alkene (0.35 g, 5.0 mmol), sealed *in vacuo* in a Pyrex tube (ca. 20 cm³) and heated at 70 °C (24 h), gave a trace of volatile material and a high-boiling liquid (1.98 g) which was shown by g.l.c. (2 m Apiezon L at 120 °C) to consist of one major component and four minor components. The major component was separated by low-pres-

sure distillation (ca. 5 mmHg) and identified as 2-(5-ethyl-5-methyl-3,3-bis(trifluoromethyl)-1-pyrazolin-1-ylidene)-1,1,1,3,3,3-hexafluoropropan-2-ide (VI; $\text{R} = \text{Et}$) * (1.78 g, 4.5 mmol, 90%) (Found: C, 33.5; H, 2.7; N, 6.9%; M^+ , 398. $\text{C}_{11}\text{H}_{10}\text{F}_{12}\text{N}_2$ requires C, 33.2; H, 2.5; N, 7.0%; M , 398), b.p. (Siwoloboff) 165 °C; λ_{max} 6.67s ($-\text{N}=\text{N}-$ str.) μm .

(d) *With 2,3-dimethylbut-1-ene.* A mixture of the azine (1.64 g, 5.0 mmol) and the alkene (0.42 g, 5.0 mmol), sealed *in vacuo* in a Pyrex tube (ca. 20 cm³) and heated at 70 °C (12 h), gave a trace of volatile material and solid material (2.05 g) which was recrystallised from light petroleum (b.p. 40–60 °C) to yield a crystalline solid identified as 1,1,1,3,3,3-hexafluoro-2-(5-isopropyl-5-methyl-3,3-bis(trifluoromethyl)-1-pyrazolin-1-ylidene)propan-2-ide (VI; $\text{R} = \text{Pr}^i$) * (1.98 g, 4.80 mmol, 96%) (Found: C, 35.1; H, 3.2; N, 6.7%; M^+ , 412. $\text{C}_{12}\text{H}_{12}\text{F}_{12}\text{N}_2$ requires C, 35.0; H, 2.9; N, 6.8%; M , 412), m.p. 47–48 °C; λ_{max} 6.67s ($-\text{N}=\text{N}-$ str.) μm .

(e) *With propene.* A mixture of the azine (3.28 g, 10.0 mmol) and propene (0.21 g, 5.0 mmol), sealed *in vacuo* in a Pyrex tube (ca. 20 cm³) and maintained at 20 °C (30 h), gave unchanged azine (2.46 g, 7.5 mmol, 75% recovered) and 4,8-dimethyl-2,2,6,6-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (II; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$) (1.03 g, 2.5 mmol, 100%), m.p. 64–65 °C (lit.,³ 63–65 °C), with n.m.r. spectrum identical with that reported.³

(f) *With but-1-ene.* A mixture of the azine (3.28 g, 10.0 mmol) and the alkene (0.28 g, 5.0 mmol), sealed *in vacuo* in a Pyrex tube (ca. 20 cm³) and maintained at 20 °C (30 h), gave unchanged azine (2.46 g, 7.5 mmol, 75% recovered) and 4,8-diethyl-2,2,6,6-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (II; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Et}$) (1.10 g, 2.5 mmol, 100%), m.p. 82.5 °C (lit.,³ 82.5 °C), with n.m.r. spectrum identical with that reported.³

A second reaction employing a 3 : 1 ratio of azine : alkene at 60 °C (24 h) gave unchanged azine (83% recovered) and the diazabicyclo[3.3.0]octane (100%).

(g) *With 3-methylbut-1-ene at 180 °C.* A mixture of the azine (4.92 g, 15.0 mmol) and the alkene (2.10 g, 30.0 mmol), heated at 180 °C (36 h), gave (i) nitrogen (0.035 g, 1.27 mmol, 9%), (ii) a mixture (0.72 g, 8.80 mmol), which was shown by i.r. spectroscopy and g.l.c. (4 m Kel-F 10 oil at 40 °C) to consist of unchanged 3-methylbut-1-ene (0.54 g, 7.70 mmol, 26% recovered) and 3,3,3-trifluoro-2-trifluoromethylprop-1-ene (IV) (0.18 g, 1.10 mmol, 4%), (iii) a higher-boiling fraction (0.3 g), which was shown by g.l.c. (2 m TTP. at 78 °C) to contain at least ten components and which was not examined further, and (iv) a residue (5.9 g), which was washed from the reaction tube with carbon tetrachloride and recrystallised from light petroleum (b.p. 40–60 °C) to give a white solid which was resublimed and identified as 4,8-di-isopropyl-2,2,6,6-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (II; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Pr}^i$) * (1.05 g, 2.25 mmol, 15%) (Found: C, 41.3; H, 4.4; N, 6.1%; M^+ , 468. $\text{C}_{16}\text{H}_{20}\text{F}_{12}\text{N}_2$ requires C, 41.0; H, 4.3; N, 6.0%; M , 468), m.p. 98.5–99.5 °C. A brown tar (4.84 g) was recovered from the recrystallisation solvent.

(h) *With 3-methylbut-1-ene at 100 °C.* A mixture of the azine (1.64 g, 5.0 mmol) and the alkene (1.05 g, 15.0 mmol), sealed *in vacuo* in a Pyrex tube (ca. 100 cm³) and heated at 100 °C (15 h), gave unchanged 3-methylbut-1-ene (0.65 g, 9.30 mmol, 62% recovered) and a residue (2.04 g) which was

⁸ J. K. Ruff, *J. Org. Chem.*, 1967, **32**, 1675.

⁹ W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, 1965, **30**, 1398.

† For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

extracted from the reaction tube with carbon tetrachloride and shown by g.l.c. (2 m DNP. at 110 °C) to consist of two components in the ratio 17 : 3. Low pressure distillation of the mixture at *ca.* 5 mmHg gave a residue of the di-isopropyl-1,5-diazabicyclo[3.3.0]octane (II; R¹ = H, R² = Pr¹) (0.35 g, 0.75 mmol, 15%) and a liquid distillate identified as 3-isopropyl-5,5-bistrifluoromethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)-3-pyrazoline (V; R = Pr¹) * (1.69 g, 4.25 mmol, 85%) (Found: C, 33.5; H, 2.7; N, 7.0%; M⁺, 398. C₁₁H₁₀F₁₂N₂ requires C, 33.2; H, 2.5; N, 7.0%; M, 398), b.p. (Siwoloboff) 169 °C; λ_{max} 2.99m (>N-H str.) and 6.03s (>C:C< str.) μm.

(j) *With 3,3-dimethylbut-1-ene.* A mixture of the azine (3.28 g, 10.0 mmol) and the alkene (0.42 g, 5.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 20 cm³) and heated at 110 °C (24 h), gave unchanged azine (1.64 g, 5.0 mmol, 50% recovered) and a residue (2.05 g) which was extracted from the reaction tube with carbon tetrachloride and recrystallised from light petroleum (b.p. 40–60 °C) to yield a white crystalline solid identified as 3-*t*-butyl-5,5-bistrifluoromethyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)-3-pyrazoline (V; R = Bu^t) * (1.98 g, 4.80 mmol, 96%) (Found: C, 35.2; H, 3.2; N, 6.9%; M⁺, 412. C₁₂H₁₂F₁₂N₂ requires C, 35.0; H, 2.9; N, 6.8%; M, 412), m.p. 54–55 °C; λ_{max} 2.98s (N-H str.) and 6.10s (>C:C< str.) μm. A non-volatile liquid (0.07 g) was recovered from the recrystallising solvent.

Reactions of the 2-Pyrazolinylpropan-2-ide (VI; R = Me).—(a) *With isobutene.* A mixture of the azomethinimine (0.96 g, 2.50 mmol) and isobutene (0.56 g, 10.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 10 cm³) and maintained at room temperature (350 h), gave unchanged isobutene (0.42 g, 7.50 mmol, 75% recovered) and a crystalline solid which was washed from the reaction tube with carbon tetrachloride and identified as 2,2,6,6-tetramethyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (II; R¹ = R² = Me) (0.11 g, 2.50 mmol, 100%).

(b) *With propene.* A mixture of the azomethinimine (1.92 g, 5.0 mmol) and propene (0.84 g, 20.0 mmol), sealed *in vacuo* in a silica tube (*ca.* 50 cm³) and maintained at 0 °C (50 h), gave unchanged propene (0.63 g, 15.0 mmol, 75% recovered) and a crystalline solid which was washed from the tube with carbon tetrachloride and identified as 4,4,8-trimethyl-2,2,6,6-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]octane (XIV) * (2.13 g, 5.0 mmol, 100%) (Found: C, 36.7;

H, 3.2; N, 6.7%; M⁺, 426. C₁₃H₁₄F₁₂N₂ requires C, 36.6; H, 3.3; N, 6.6%; M, 426), m.p. 60–61 °C.

(c) *Flow pyrolysis.* The azomethinimine (0.96 g, 2.50 mmol), passed at low pressure (1 mmHg) through a Pyrex tube maintained at 400 °C (1 h; contact time 2.3 s), gave (i) unchanged azomethinimine (0.12 g, 0.30 mmol, 12% recovered), (ii) isobutene (0.12 g, 2.20 mmol, 100%), and (iii) hexafluoroacetone azine (0.72 g, 2.20 mmol, 100%).

Reactions of the 3-Isopropyl-3-pyrazoline (V; R = Pr¹).—(a) *With 3-methylbut-1-ene.* A mixture of the pyrazoline (0.80 g, 2.0 mmol) and the alkene (0.70 g, 10.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 20 cm³) and heated at 120 °C (120 h), gave quantitative recoveries of unchanged reactants.

(b) *Flow pyrolysis.* The adduct (0.60 g, 1.50 mmol), passed at low pressure (1 mmHg), through a Pyrex tube maintained at 450 °C (30 min; contact time 1.7 s), gave (i) unchanged adduct (0.08 g, 0.29 mmol, 13% recovered), (ii) 1,1,1,3,3,3-hexafluoro-2-trifluoromethylpropane (XVI) (0.29 g, 1.30 mmol, 100%) (Found: M, 222. Calc. for C₄HF₆: M, 220), and (iii) 3-isopropyl-5-trifluoromethylpyrazole (XVII) * (0.23 g, 1.30 mmol, 100%) (Found: C, 46.9; H, 5.2; N, 15.4%; M⁺, 178. C₇H₉F₃N₂ requires C, 47.2; H, 5.1; N, 15.7%. M, 178), m.p. 129–130 °C.

Flow Pyrolysis of the 2-Pyrazolinylpropan-2-ide (VI; R = Et).—The azomethinimine (1.0 g, 2.50 mmol), passed at low pressure (1 mmHg) through a Pyrex tube maintained at 400 °C (1 h; contact time 2.3 s), gave unchanged azomethinimine (0.08 g, 0.20 mmol, 8% recovered), 2-methylbut-2-ene (0.16 g, 2.30 mmol, 100%), and hexafluoroacetone azine (0.76 g, 2.30 mmol, 100%).

Pyrolysis of the Di-isopropyl-1,5-diazabicyclo[3.3.0]octane (II; R¹ = H, R² = Pr¹).—The adduct (0.60 g, 1.28 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 100 cm³) and heated at 190 °C (24 h), gave (i) 3,3,3-trifluoro-2-trifluoromethylprop-1-ene (IV) (0.25 g, 1.52 mmol, 85%) (Found: M, 165. Calc. for C₄H₂F₆: M, 164), (ii) a higher-boiling fraction (0.60 g), which was shown by g.l.c. (2 m Silicone MS 550 oil at 75 °C) to contain at least six components, and (iii) a residue (0.29 g), which was extracted from the reaction tube with carbon tetrachloride and recrystallised from light petroleum (b.p. 40–60 °C) to give unchanged adduct (0.18 g, 0.38 mmol, 30% recovered). A viscous tar (0.11 g) was recovered from the recrystallisation solvent.

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