

Unsaturated Nitrogen Compounds containing Fluorine. Part V.¹ Reactions of Hexafluoroacetone Azine with Open-chain and Cyclic Hydrocarbon Dienes²

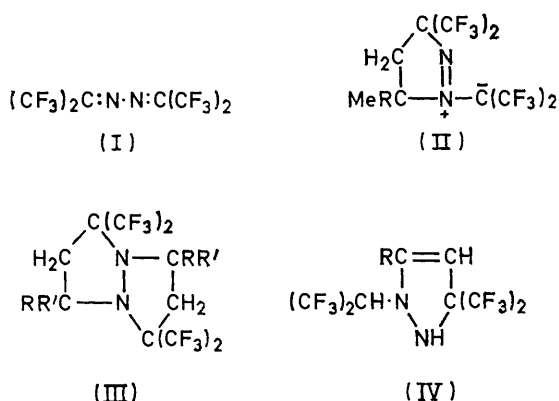
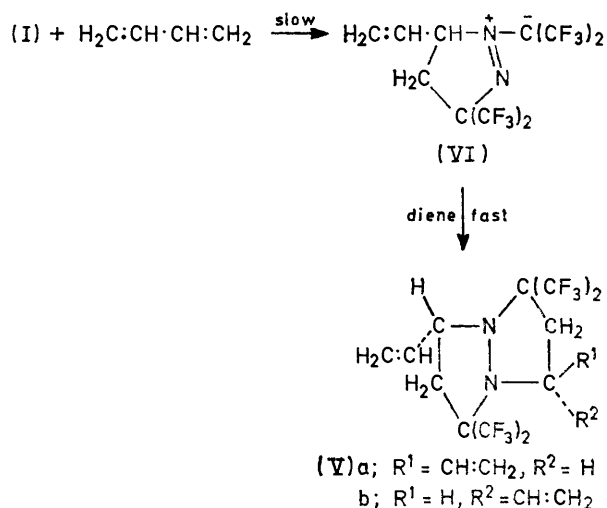
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The reactions of hexafluoroacetone azine with the dienes $\text{CH}_2\text{:CR}^1\text{-CR}^2\text{:CH}_2$ ($\text{R}^1 = \text{R}^2 = \text{H}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{R}^2 = \text{Me}$), cyclopentadiene, and norbornadiene proceed mainly *via* azomethineimine intermediates formed by 1,3-dipolar addition of the azine to a double bond in the diene; the reaction with 2,3-dimethylbuta-1,3-diene also gives the Diels-Alder adduct in low yield (8%). All the azomethineimines, except that formed from 2,3-dimethylbuta-1,3-diene which is readily isolated, react further with an excess of diene to afford 'criss-cross' adducts. The azomethineimine derived from cyclopentadiene can be isolated if an excess of azine is used in the reaction, but that formed from norbornadiene undergoes homopolymerisation. A small-scale static pyrolysis of the buta-1,3-diene criss-cross adduct at 210–230 °C affords 3,3,3-trifluoro-2-trifluoromethylpropene, *cis*- and *trans*-*N*-(prop-1-enyl)pyrazole, and *N*-[1,1-bis(trifluoromethyl)pent-3-enyl]pyrazole, but a larger-scale (higher pressure) pyrolysis also gives *N*-(3,3,3-trifluoro-2-trifluoromethylpropyl)pyrazole.

THE reaction of hexafluoroacetone azine (I) with olefins of the type $\text{H}_2\text{C:CMeR}$ ($\text{R} = \text{Me}$, Et , or Pr^i) gives isolable azomethineimines (II), which can react further with an excess of olefin to afford 'criss-cross' 2:1 adducts (III; $\text{R}' = \text{Me}$).^{1,3} However, with olefins of type $\text{H}_2\text{C:CHR}$ the products are Δ^3 -pyrazolines (IV; $\text{R} = \text{Pr}^i$ or Bu^t)¹ or criss-cross adducts (III; $\text{R} = \text{H}$, Me , or Et , $\text{R}' = \text{H}$).^{1,4,5} The results of an investigation into the reactions of the azine (I) with buta-1,3-diene, 2-methylbuta-1,3-diene, 2,3-dimethylbuta-1,3-diene, cyclopentadiene, norbornadiene, and allene are now reported.

A mixture of buta-1,3-diene and the azine (I) (2:1 molar ratio), maintained at room temperature (24 h), gave unchanged diene (11%), unchanged azine (11%), and a mixture (100%) of *cis*- and *trans*-2,2,6,6-tetrakis(trifluoromethyl)-4,8-divinyl-1,5-diazobicyclo[3.3.0]-octane (V). The two isomers gave identical mass spectra and the major product, considered to be the

the suspected azomethineimine intermediate (VI) the reaction was repeated with an excess of azine (I) at room temperature, but again a mixture (100%) of isomers (Va and b) (in the ratio 4:1) was obtained, together with the excess of azine (I).



trans-isomer (Va) (80%) on steric grounds, was separated by repeated extraction with acetone; the *cis*-isomer (Vb) was not obtained pure. In an attempt to isolate

Similarly, the reaction of the azine (I) with isoprene (1:2 molar ratio) at 40 °C (6 h), gave unchanged azine (2%), unchanged diene (2%), and a mixture (100%) of three criss-cross 2:1 adducts in the ratio 3:9:5. We could not assign structures to the products; six criss-cross 2:1 adducts are possible owing to the non-equivalence of the vinyl groups in the diene.

In contrast to these reactions a mixture of 2,3-dimethylbuta-1,3-diene and the azine (I) (2:1 molar ratio), heated at 40 °C (24 h), gave unchanged azine (3%), unchanged diene (51%), the azomethineimine

¹ Part IV, S. E. Armstrong and A. E. Tipping, *J.C.S. Perkin I*, 1975, 538.

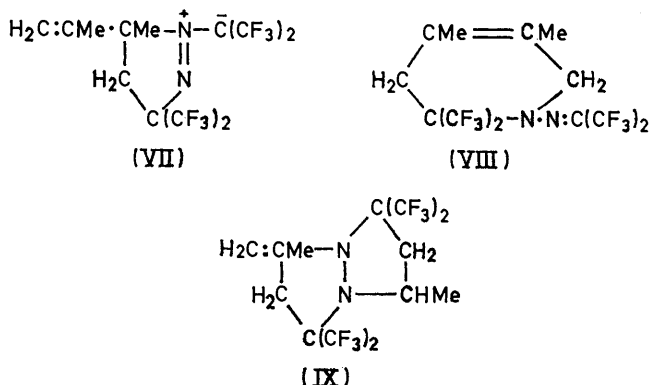
² Preliminary communication, S. E. Armstrong and A. E. Tipping, *J. Fluorine Chem.*, 1973, 3, 119.

³ 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.

⁴ T. P. Forshaw and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 2404.

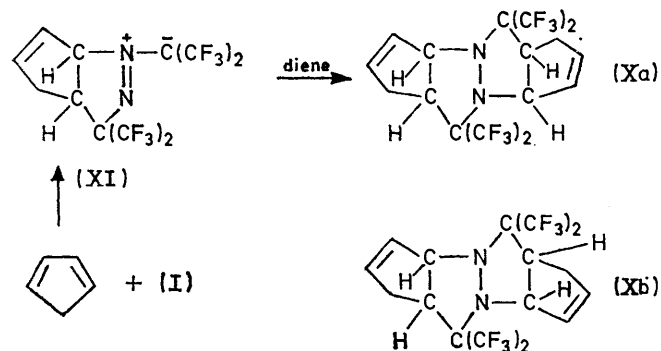
⁵ S. E. Armstrong and A. E. Tipping, unpublished results.

(VII) (91%), and the Diels–Alder adduct (VIII) (8%). The major adduct (VII) on flow pyrolysis at 350 °C decomposed (84%) to give the azine (I) and 2,3-dimethylbuta-1,3-diene in quantitative yields, but the minor adduct (VIII) was unchanged under the same conditions. The adduct (VII) reacted slowly with



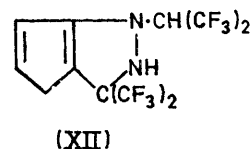
propene at 0 °C to give the criss-cross adduct (IX) (100%), but it did not react with 2,3-dimethylbuta-1,3-diene even at 80 °C, presumably because of increased steric hindrance in the diene relative to propene.

The reaction between the azine (I) and cyclopentadiene (1 : 2 molar ratio) at 20 °C (6 h) gave unchanged diene (9%) and a mixture (96%) of the *cis*- and *trans*-criss-cross 2 : 1 adducts (Xa and b) in the ratio 1 : 5. However, the reaction of an excess of azine (I) with the diene (3 : 1 molar ratio) at 0 °C (30 h) gave unchanged azine (70%), the criss-cross adduct (X) (16%), and the azomethineimine (XI) (80%), which reacted with an excess of diene at room temperature to give a mixture (100%) of the criss-cross adducts (Xa and b) in the ratio 1 : 5.

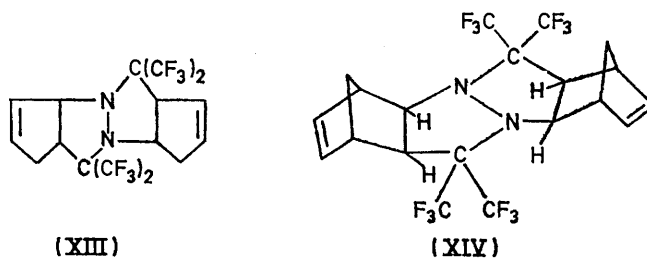


The azomethineimine (XI) is the first such intermediate formed from the azine (I) to be isolated which contains hydrogen atoms on both C-4 and C-5 of the heterocycle. Previously isolated azomethineimines (II; R = Me, Et, or Prⁱ)^{1,3} contained two alkyl groups on C-5 of the heterocycle. Olefins of type CH₂:CHR (R = Prⁱ or Bu^t) reacted with the azine (I) to afford Δ³-pyrazolines (IV), possibly *via* rearrangement of intermediate azomethineimines analogous to (XI). The adduct (XI) was

stable at 0 °C but at room temperature it slowly darkened and formed higher-boiling material; the Δ³-pyrazoline (XII) was not detected and it is probable that the product was polymeric, arising *via* intermolecular 1,3-dipolar attack on the olefinic double bond of a second molecule.



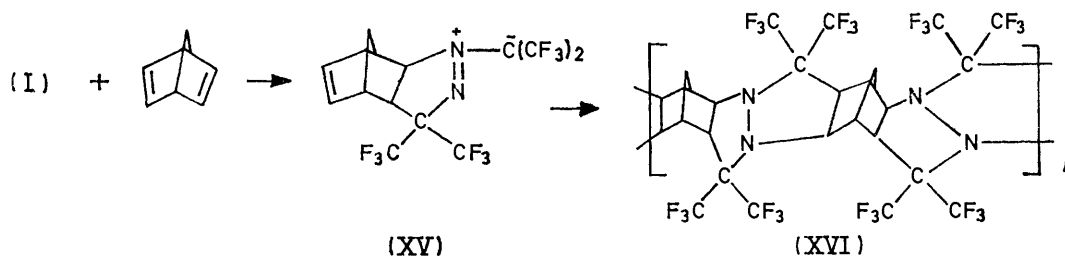
The possibility that the criss-cross adducts had the alternative structure (XIII) is considered to be less likely because both isomers gave the same mass spectrum and the ¹H n.m.r. spectrum of the separated major isomer showed bands at τ 4.22 (2H, vinylic), 5.73 (1H, CH), 6.45 (1H, q, CH), and 7.25 (2H, CH₂); the lowest field absorption (τ 5.73) for the tertiary protons would be expected for CH·N and so the other (τ 6.45) is assigned to (CF₃)₂C·CH [the splitting (q) also shows that it is adjacent to the CH₂ group (*J*_{H,H} ≈ *J*_{H,CH} = 8.4 Hz)].



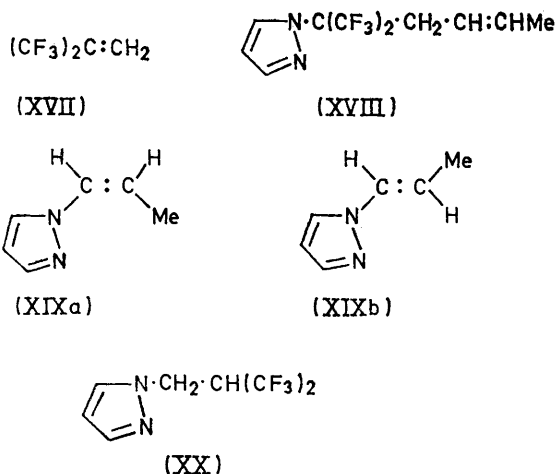
The reaction of norbornadiene with the azine (I) (3 : 1 molar ratio) at room temperature (12 h) gave unchanged diene (29%) and a criss-cross 2 : 1 adduct (99%), apparently present as one isomer (g.l.c.), probably the *exo,exo*-isomer (XIV). However, the reaction of a 2 : 1 azine–diene mixture at 20 °C (24 h) gave unchanged azine (50%) and a 1 : 1 copolymer (100%), the mass spectrum of which showed peaks at *m/e* > 2 500. The polymer was insoluble in common solvents and, since criss-cross adducts are formed when an excess of olefin is used, presumably *via* the azomethineimine (XV), it is probable that the polymer is formed by homopolymerisation of the azomethineimine (XV) and has the structure (XVI).

When the azine (I) was treated with allene (1 : 2 molar ratio) at 80 °C the reactants were unchanged, but prolonged heating at 150 °C (72 h) afforded unchanged azine (41%), unchanged allene (64%), nitrogen (30%), and a viscous tar which did not yield any volatile material on attempted low-pressure distillation.

All the products obtained from the reactions of the azine (I) with the various dienes, except the Diels–Alder adduct (VIII), can be explained on the basis of azomethineimine intermediates. Thus the open-chain dienes, buta-1,3-diene and isoprene, react analogously to the



olefins of type $\text{CH}_2\text{:CHR}$ ($\text{R} = \text{H, Me, or Et}$)^{1,4} and give exclusively criss-cross adducts; with 2,3-dimethyl-

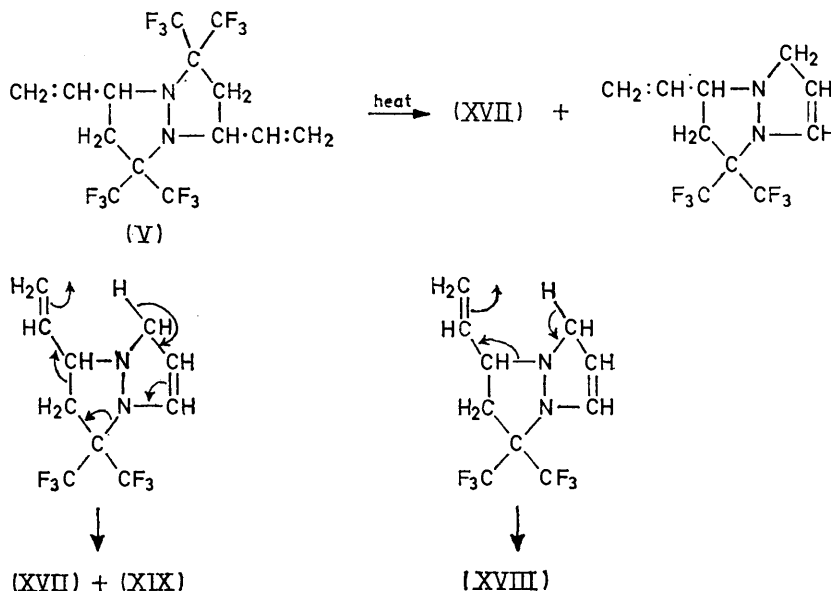


buta-1,3-diene the reaction of the intermediate azomethineimine with the diene is sterically hindered and

norbornadiene with further diene are also apparently hindered sterically to some extent. Unlike the reactions of the azine (I) with the olefins $\text{CH}_2\text{:CHR}$ ($\text{R} = \text{Pr}^i$ or Bu^t)¹ and cyclopentene,^{2,5} evidence was not obtained in the present work for the formation of Δ^3 -pyrazolines.

Pyrolysis of the criss-cross adduct (V) formed with buta-1,3-diene in a sealed tube at 230 °C gave nitrogen (trace), 3,3,3-trifluoro-2-trifluoromethylpropene (XVII) (85%), *N*-(1,1-bistrifluoromethylpent-3-enyl)pyrazole (XVIII) (19%), *cis*-*N*-(prop-1-enyl)pyrazole (XIXa) (32%), the corresponding *trans*-isomer (XIXb) (4%), and a viscous tar; pyrolysis at a slightly lower temperature (210 °C) gave (XVII) (83%), (XVIII) (33%), and a mixture (67%) of (XIXa) and (XIXb). However, a large-scale pyrolysis at 230 °C gave (XVII) (71%), (XVIII) (9%), (XIXa) (12%), (XIXb) (13%), and *N*-(3,3,3-trifluoro-2-trifluoromethylpropyl)pyrazole (XX) (10%). The olefins (XIXa and b) have previously been prepared⁶ by the decomposition of 1,1-di-(pyrazol-1-yl)propane, but the isomers were not separated.

The products (XVII)—(XIX) are considered to be



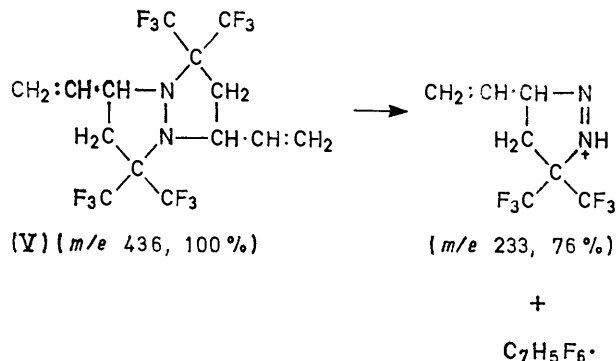
SCHEME 1

the azomethineimine can be isolated, *cf.* olefins of type $\text{H}_2\text{C:CMER}$ ($\text{R} = \text{Me or Et}$).^{1,3} The reactions of the azomethineimines formed from cyclopentadiene and

formed as shown in Scheme 1. The observation that compound (XX) was formed only in the larger-scale

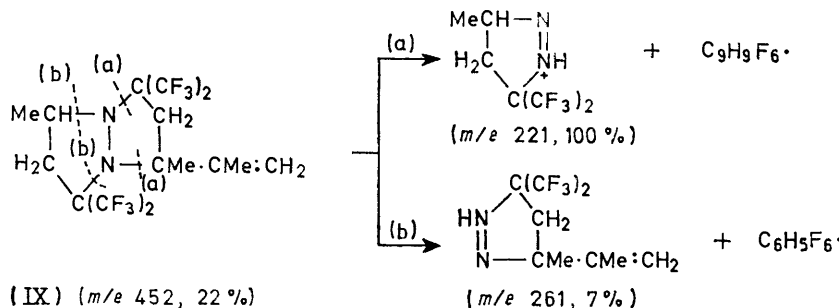
⁶ S. Trofimenko, *J. Org. Chem.*, 1970, **35**, 3459.

reaction, *i.e.* the reaction that gave a *higher* pressure of olefin (XVII), indicates that it probably arises *via* reaction of olefin (XVII) with the pyrazole derivatives (XVIII) and/or (XIX), *e.g.* $(\text{CF}_3)_2\text{C}:\text{CH}_2 + (\text{XIX}) \rightarrow (\text{XX}) + [\text{C}_3\text{H}_4] \rightarrow \text{tar}$.

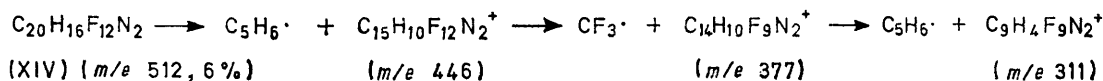


SCHEME 2

Structures of the Products.—These were established by mass spectrometry and n.m.r. spectroscopy; * interesting or general spectral observations are discussed.



SCHEME 3



SCHEME 4

(a) *Criss-cross 2:1 adducts.* The mass spectra of the adducts all showed intense parent ion peaks and, with the exception of that derived from norbornadiene (XIV), intense or base peaks corresponding to fission of two C-N bonds in one half of the molecule (Scheme 2). The mixed adduct (IX) decomposed by both possible routes (Scheme 3).

The same type of breakdown has been observed previously in the spectra of the criss-cross adducts derived from olefins of type $\text{H}_2\text{C}:\text{CHR}$ ($\text{R} = \text{H}, \text{Me}, \text{or Et}$).⁴ The spectrum of the adduct (XIV) did not contain a peak at m/e 243 corresponding to the above typical breakdown, but peaks were observed at m/e 446

* Data are available as Supplementary Publication No. SUP 21367 (12 pp., 1 microfiche). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

(7%), 377 (100%), and 311 (43%) indicating the ready loss of cyclopentadiene from the molecule (Scheme 4).

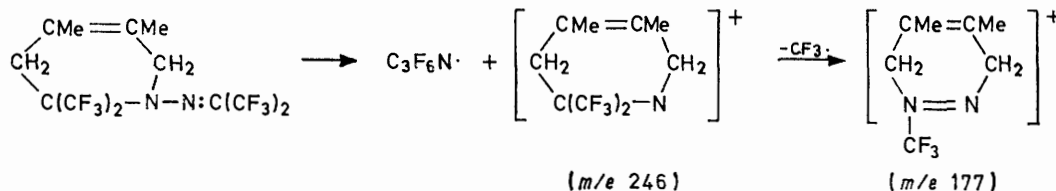
The n.m.r. spectra were all consistent with the proposed structures.

(b) *Azomethineimines.* The mass spectra of both isopropylides (VII) and (XI) showed peaks corresponding to breakdown of the molecules into the compounds from which they were formed, *i.e.* azine (I) at m/e 328 (*ca.* 12%) and the dienes C_6H_{10} at m/e 82 (54%) or C_5H_6 at m/e 66 (67%). The ^{19}F n.m.r. spectra showed bands at -26.0 (3F, q, J 8.8 Hz), -11.6 (3F, q), and -5.1 p.p.m. (6F, s) for compound (XII) and at -23.7 (3F, q, J 10.8 Hz), -11.6 (3F, q), -10.1 (3F, q, J 7.9 Hz), and -3.3 p.p.m. (3F, q) for compound (XI), assigned to the non-equivalent CF_3 groups in the $(\text{CF}_3)_2\text{C}^-\text{N}^+=\text{N}- \leftrightarrow (\text{CF}_3)_2\text{C}=\text{N}^+-\text{N}^-$ and $(\text{CF}_3)_2\text{C}$, respectively, *cf.* azomethineimines formed from olefins of type $\text{CH}_2:\text{CMeR}$ ($\text{R} = \text{Me}, \text{Et}, \text{or Pr}^i$) with ^{19}F n.m.r. bands at *ca.* -26 (3F, q, J 8.5 to 9 Hz), *ca.* -12 (3F, q), and *ca.* -5 p.p.m. (6F).¹ The ^1H n.m.r. absorption due to $\text{CH}-\text{N}^+$ in the azomethineimine (XI) was, as expected, at very low field (τ 4.0).

(c) *Diels-Alder adduct (VIII).* The mass spectrum of the adduct showed a parent ion peak at m/e 410 (10%) and intense peaks at m/e 246 (55%) and 177 (65%) corresponding to loss of $(\text{CF}_3)_2\text{C}=\text{N}-$ and a further loss of $\text{CF}_3\cdot$ to give the dihydropyridine ring system, respectively (Scheme 5). The ^{19}F n.m.r. spectrum was similar to those of the azomethineimines and contained absorptions at -23.4 (3F, q, J 9.4 Hz), -12.0 (3F, q), and -5.9 p.p.m. (6F), assigned to the non-equivalent CF_3 groups in $(\text{CF}_3)_2\text{C}=\text{N}$ and $(\text{CF}_3)_2\text{C}$, respectively.

(d) *N-Substituted pyrazoles.* The mass spectra of the *N*-(prop-1-enyl)pyrazoles (XIXa and b) contained strong parent ion peaks at m/e 108 and base peaks at m/e 81, corresponding to loss of HCN from the parent ions. Although the mass spectra of the *N*-substituted pyrazoles (XVIII) and (XX) showed strong parent ion peaks at m/e 272 and 232, respectively, base peaks were observed

at m/e 68 [compound (XVIII)], corresponding to the pyrazole ion $\overline{\text{N}:\text{CH}:\text{CH}:\text{CH}:\text{N}^+}$, and m/e 81 [compound (XX)], corresponding to the resonance-stabilised ion $\overline{\text{N}:\text{CH}:\text{CH}:\text{CH}:\text{N}^+\cdot\text{CH}_2}$ or $\overline{^+\text{N}:\text{CH}:\text{CH}:\text{CH}:\text{N}:\text{CH}_2}$; the spectrum of compound (XX) also contained a strong peak at m/e 68. The ^1H n.m.r. spectra of compounds (XVIII) and (XX) showed the typical pyrazole ring



SCHEME 5

proton patterns, but it was not possible to determine whether compound (XVIII) was the *cis*- or the *trans*-isomer.

EXPERIMENTAL

Techniques used were mainly as described previously.⁷ Thermal reactions of hexafluoroacetone azine were carried out *in vacuo* in sealed Pyrex tubes (*ca.* 300 cm³ unless stated otherwise). Separations by g.l.c. employed the following columns: Carbowax, Silicone SE 30 oil, Apiezon L (APL), tritosyl phosphate (TTP), or polyethylene glycol adipate (PEGA) (20%) on Celite. N.m.r. spectra were run with external trifluoroacetic acid and internal tetramethylsilane as ¹⁹F and ¹H references, respectively.

Hexafluoroacetone azine was prepared by treatment of the corresponding imine with potassium fluoride and bromine⁸ followed by irradiation of the resultant imine,⁹ or by treatment of hexafluoroacetone with an excess of hydrazine hydrate followed by dehydration of the resultant 2:1 adduct with phosphoryl chloride.¹⁰

Reactions of Hexafluoroacetone Azine with Dienes.—
(a) *Buta-1,3-diene*. A mixture of the azine (3.94 g, 12.0 mmol) and the diene (1.30 g, 24.0 mmol), maintained at room temperature (24 h), gave (i) unchanged diene (0.14 g, 2.6 mmol, 11% recovered), (ii) unchanged azine (0.43 g, 1.3 mmol, 11% recovered), and (iii) a solid residue which was washed out with hot carbon tetrachloride and identified as a mixture of *cis*- and *trans*-criss-cross 2:1 adducts (4.66 g, 10.7 mmol, 100%) in the ratio 1:4 by g.l.c. (2 m Carbowax at 102 °C) and g.l.c.–mass spectrometry. The major isomer was isolated from the mixture by repeated extraction with acetone and identified as 2,2,6,6-tetrakis(trifluoromethyl)-*trans*-4,8-divinyl-1,5-diazabicyclo[3.3.0]octane (Va) (3.73 g, 8.56 mmol, 80%) (Found: C, 38.8; H, 2.8; N, 6.3%; M^+ , 436. C₁₄H₁₂F₁₂N₂ requires C, 38.5; H, 2.7; N, 6.4%; M , 436, m.p. 89–90 °C; λ_{max} , 6.07 μm (C:C str.).

In a second experiment, a mixture of the azine (3.94 g, 12.0 mmol) and the diene (0.27 g, 5.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 100 cm³) and maintained at room temperature (12 h), gave unchanged azine (3.11 g, 9.5

mmol, 79% recovered) and a mixture (1.09 g, 2.5 mmol, 100%) of *cis*- and *trans*-adducts (Vb and a) in the ratio 1:4.

(b) *2-Methylbuta-1,3-diene*. A mixture of the azine (3.94 g, 12.0 mmol) and the diene (1.63 g, 24.0 mmol), heated at 40 °C (6 h), gave (i) unchanged diene (0.05 g, 0.74 mmol, 3% recovered), (ii) unchanged azine (0.07 g, 0.20 mmol, 2% recovered), and (iii) a solid residue (5.45 g) which was extracted with hot carbon tetrachloride and shown by g.l.c. (2 m Apiezon L at 90 °C) to consist of three

components in the ratio 3:9:5. The mixture was identified by g.l.c.–mass spectrometry as consisting of 2:1 (diene–azine) adducts (5.45 g, 11.8 mmol, 100%) (Found: C, 41.4; H, 3.5; N, 5.9%; M^+ , 464. Calc. for C₁₆H₁₆F₁₂N₂: C, 41.4; H, 3.5; N, 6.0%; M , 464), λ_{max} , 6.03s μm (C:C str.), but attempted separation by column chromatography (alumina and silica gel packed columns) was unsuccessful, as was attempted separation by g.l.c., because of partial decomposition of the adducts on the column.

(c) *2,3-Dimethylbuta-1,3-diene*. A mixture of the azine (3.94 g, 12.0 mmol) and the diene (1.97 g, 24.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 100 cm³) and heated at 40 °C (24 h), gave (i) unchanged diene (1.0 g, 12.2 mmol, 51% recovered), (ii) unchanged azine (0.1 g, 0.31 mmol, 3% recovered), and (iii) a residue (4.81 g) which was washed out with hot carbon tetrachloride. Recrystallisation of the residue from petroleum (b.p. 40–60 °C), gave a crystalline solid identified as 1-[5-isopropenyl-5-methyl-3,3-bis(trifluoromethyl)- Δ^1 -pyrazolin-1-yl]-2,2-trifluoro-1-trifluoromethylethanide (VII) (4.40 g, 10.7 mmol, 91%) (Found: C, 35.5; H, 2.5; F, 55.2; N, 6.9%; M^+ , 410. C₁₂H₁₀F₁₂N₂ requires C, 35.2; H, 2.4; F, 55.6; N, 6.8%; M , 410, m.p. 39–40 °C; λ_{max} , 6.06 μm (C:C str.).

Removal of the recrystallisation solvent from the filtrate, followed by low pressure distillation (*ca.* 2 mmHg) of the resultant material gave a residue of tar (0.04 g) and a distillate identified as 1,2,3,6-tetrahydro-4,5-dimethyl-2,2-bis(trifluoromethyl)-1-(2,2-trifluoro-1-trifluoromethylethylidene-amino)pyridine (VIII) (0.37 g, 0.90 mmol, 8%) (Found: C, 35.4; H, 2.6; N, 6.9%; M^+ , 410. C₁₂H₁₀F₁₂N₂ requires C, 35.2; H, 2.4; N, 6.8%; M^+ , 410), b.p. (Siwoloboff) 208 °C at 740 mmHg; λ_{max} , 6.17s μm (C:C str.).

(d) *Cyclopentadiene*. A mixture of the azine (3.94 g, 12.0 mmol) and the diene (1.58 g, 24.0 mmol), maintained at room temperature (6 h), gave unchanged diene (0.15 g, 2.27 mmol, 9% recovered) and a residue (5.37 g) which was washed out with acetone. Recrystallisation from carbon tetrachloride afforded a crystalline solid (5.3 g) and, after removal of the solvent, a liquid (0.07 g) which was not investigated further. G.l.c. examination (2 m Carbowax at 165 °C) of the solid showed that it consisted of two

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

¹⁰ K. Burger, J. Fehn, and W. Thenn, *Angew. Chem.*, 1973, **85**, 541.

⁷ S. E. Armstrong and A. E. Tipping, *J.C.S. Perkin I*, 1974, 2716.

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

components in the ratio 1:5 which had identical mass spectra (g.l.c.-mass spectrometry) and were identified as *cis*- (Xa) and *trans*- (Xb) 2:1 criss-cross adducts (5.3 g, 11.53 mmol, 96%) (Found: C, 42.0; H, 2.7; F, 49.2; N, 5.9%; M^+ , 460. Calc. for $C_{16}H_{12}F_{12}N_2$: C, 41.7; H, 2.6; F, 49.5; N, 6.1%; M , 460). Repeated extraction of the mixture with acetone gave a pure sample of the major isomer *trans*-7,7,14,14-tetrakis(trifluoromethyl)-1,8-diazatetracyclo[6.6.0.0.2,6^{0,9,13}]tetradeca-3,10-diene (Xb) (4.42 g, 9.61 mmol, 80%) (Found: C, 42.0; H, 2.7; N, 5.9%; M^+ , 460), m.p. 149–150 °C; λ_{\max} , 6.14 μm (C:C str.). A pure sample of the *cis*-isomer (Xa) (0.88 g, 1.92 mmol, 16%) could not be obtained from the mixture and so it was not examined further.

In a second experiment a mixture of the azine (4.92 g, 15.0 mmol) and the diene (0.33 g, 5.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 50 cm^3) and maintained at 0 °C (30 h), gave (i) unchanged azine (3.45 g, 10.5 mmol, 70% recovered), (ii) an involatile liquid (1.57 g), (iii) criss-cross 2:1 adduct (0.18 g, 0.40 mmol, 16%), and (iv) tar (0.05 g). The involatile liquid was shown by g.l.c. (2 m PEGA at 140 °C) to consist of one component identified as 2,2,2-trifluoro-1-[3,3a,4,6a-tetrahydro-3,3-bis(trifluoromethyl)cyclopentapyrazol-1-*io*]-1-trifluoromethylethanide (XI) (1.57 g, 4.0 mmol, 80%) (Found: C, 33.2; H, 1.8; N, 6.8. $C_{11}H_6F_{12}N_2$ requires C, 33.5; H, 1.5; N, 7.1%; λ_{\max} , 6.54s and 6.86 μm (typical of isopropylides).

(e) *Norbornadiene*. A mixture of the azine (3.28 g, 10.0 mmol) and the diene (2.76 g, 30.0 mmol), maintained at room temperature (12 h), gave unchanged norbornadiene (0.80 g, 8.7 mmol, 29% recovered) and a residue which was washed out with acetone and recrystallised from carbon tetrachloride to yield a crystalline solid (5.02 g) and after removal of the solvent a high-boiling liquid (0.22 g) which was not examined further. The crystalline solid was shown by g.l.c. (2 m SE 30 at 200 °C) to consist of one component identified as 3,3,11,11-tetrakis(trifluoromethyl)-4,12-diazahexacyclo[12.2.1.1.5,9^{0,2},13^{0,4},12^{0,5,10}]octadeca-7,15-diene (XIV) (5.02 g, 9.8 mmol, 98%) (Found: C, 46.8; H, 3.2; N, 5.5%; M^+ , 512. $C_{20}H_{16}F_{12}N_2$ requires C, 46.8; H, 3.1; N, 5.5%; M , 512), m.p. 171–172 °C.

In a second experiment a mixture of the azine (3.28 g, 10.0 mmol) and norbornadiene (0.46 g, 5.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 20 cm^3) and maintained at room temperature (24 h), gave unchanged azine (1.64 g, 5.0 mmol, 50% recovered) and an *azine-norbornadiene* 1:1 copolymer (XVI) (2.10 g, 5.0 mmol, 100%) [Found: C, 37.3; H, 2.0; N, 6.8. ($C_{13}H_8F_{12}N_2$)_n requires C, 37.1; H, 1.9; N, 6.7%] which was insoluble in common solvents.

(f) *Allene*. A mixture of the diene (3.28 g, 10.0 mmol) and allene (0.80 g, 20.0 mmol), heated at 150 °C (72 h), gave (i) nitrogen (0.05 g, 1.74 mmol, 30%; M , 27), (ii) unchanged allene (0.51 g, 12.8 mmol, 64% recovered), (iii) unchanged azine (1.35 g, 4.1 mmol, 41% recovered), and (iv) a viscous tar (2.16 g) which did not yield any volatile fraction on attempted low-pressure distillation. An attempted reaction carried out at 80 °C (24 h) gave only unchanged reactants.

*Reactions of 1-[5-Isopropenyl-5-methyl-3,3-bis(trifluoromethyl)- Δ^1 -pyrazolin-1-*io*]-2,2,2-trifluoro-1-trifluoromethylethanide (VII).*—(a) *With propene*. A mixture of the adduct (0.82 g, 2.0 mmol) and propene (0.21 g, 5.0 mmol), maintained at 0 °C (200 h), gave unchanged propene (0.13 g, 3.0 mmol, 60% recovered) and a crystalline solid identified as 4-isopropenyl-4,8-dimethyl-2,2,6,6-tetrakis(trifluoro-

methyl)-1,5-diazabicyclo[3.3.0]octane (IX) (0.90 g, 2.0 mmol, 100%) (Found: C, 39.8; H, 3.6; N, 6.2%; M^+ , 452. $C_{15}H_{16}F_{12}N_2$ requires C, 39.8; H, 3.5; N, 6.2%; M , 452), m.p. 40–41 °C; λ_{\max} , 6.10s μm (C:C str.).

(b) *With 2,3-dimethylbuta-1,3-diene*. A mixture of the adduct (2.05 g, 5.0 mmol) and the diene (0.82 g, 10.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 10 cm^3) and heated at 80 °C (50 h), gave only a mixture (2.87 g, 100% recovered) of unchanged azine and low polymer derived from the diene.

(c) *Flow pyrolysis*. The adduct (1.03 g, 2.50 mmol), passed at low pressure (1 mmHg) through a Pyrex tube heated at 350 °C (1 h; contact time 2.6 s), gave hexafluoroacetone azine (0.69 g, 2.10 mmol, 100%), 2,3-dimethylbuta-1,3-diene (0.17 g, 2.10 mmol, 100%), and unchanged adduct (0.17 g, 0.40 mmol, 16% recovered).

Reactions of 2,2,6,6-Tetrakis(trifluoromethyl)-4,8-divinyl-1,5-diazabicyclo[3.3.0]octane (V).—(a) *With hexafluoroacetone azine*. A mixture of the 2:1 adduct (0.87 g, 2.0 mmol) and the azine (3.2 g, 10.0 mmol), sealed in a Pyrex tube (*ca.* 10 cm^3) and heated at 80 °C (100 h), gave only unchanged reactants.

(b) *Pyrolysis*. The adduct (0.96 g, 2.2 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 100 cm^3) and heated at 230 °C (26 h), gave (i) nitrogen (trace), (ii) 3,3,3-trifluoro-2-trifluoromethylpropene (XVII) (0.62 g, 3.75 mmol, 85%), (iii) a higher-boiling fraction (0.20 g), and (iv) a mixture (0.13 g) of a viscous tar and solid material. The three components of the involatile fraction, present in the ratio 5:9:1, were separated by g.l.c. and identified as *N*-[1,1-bis(trifluoromethyl)pent-3-enyl]pyrazole (XVIII) (0.114 g, 0.42 mmol, 19%) (Found: C, 44.1; H, 3.7; N, 10.2%; M^+ , 272. $C_{10}H_{10}F_6N_2$ requires C, 44.2; H, 3.8; N, 9.9%; M , 272), λ_{\max} , 6.54 μm (cyclic C:C:C:N); *cis-N*-(prop-1-enyl)pyrazole (XIXa) (0.075 g, 0.70 mmol, 32%) (Found: C, 66.7; H, 7.3; N, 25.6%; M^+ , 108. $C_8H_8N_2$ requires C, 66.7; H, 7.4; N, 25.9%; M , 108), λ_{\max} , 5.98s (C:C str.) and 6.60s μm (cyclic C:C:C:N); and *trans-N*-(prop-1-enyl)pyrazole (XIXb) (0.010 g, 0.08 mmol, 4%) (Found: C, 66.7; H, 7.4; N, 25.7%; M^+ , 108), λ_{\max} , 5.95s (C:C str.) and 6.60s μm (C:C:C:N).

In a second experiment the adduct (6.55 g, 15.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 200 cm^3) and heated at 230 °C (26 h), gave (i) nitrogen (trace), (ii) 3,3,3-trifluoro-2-trifluoromethylpropene (XVII) (3.47 g, 21.2 mmol, 71%), (iii) a higher-boiling fraction (1.10 g), and (iv) a mixture (1.97 g) of viscous tar and solid material. The higher-boiling fraction was separated by g.l.c. (as above) into its four components present in the ratio 5:4:6:6 and identified as *N*-(3,3,3-trifluoro-2-trifluoromethylpropyl)pyrazole (XX) (0.355 g, 1.53 mmol, 10%) (Found: C, 36.0; H, 2.6; N, 11.7%; M^+ , 232. $C_7H_8F_6N_2$ requires C, 36.2; H, 2.6; N, 12.0%; M , 232), λ_{\max} , 6.58 μm (C:C:C:N); *N*-[1,1-bis(trifluoromethyl)pent-3-enyl]pyrazole (XVIII) (0.345 g, 1.27 mmol, 9%); *cis-N*-(prop-1-enyl)pyrazole (XIXa) (0.195 g, 1.80 mmol, 12%); and *trans-N*-(prop-1-enyl)pyrazole (XIXb) (0.205 g, 1.90 mmol, 13%).

In a third experiment the adduct (0.66 g, 1.50 mmol), heated at 210 °C (24 h), gave (i) 3,3,3-trifluoro-2-trifluoromethylpropene (XVII) (0.41 g, 2.50 mmol, 83%), (ii) *N*-[1,1-bis(trifluoromethyl)pent-3-enyl]pyrazole (XVIII) (0.14 g, 0.50 mmol, 33%), and (iii) a mixture (0.11 g, 1.0 mmol, 67%) of *cis*- and *trans-N*-(prop-1-enyl)pyrazole (XIX).

Reaction of the Isopropylide (XI) with Cyclopentadiene.—

A mixture of the isopropylide (0.39 g, 1.0 mmol) and cyclopentadiene (0.26 g, 4.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 20 cm³) and maintained at room temperature (5 h), gave (i) unchanged cyclopentadiene (0.19 g, 2.9 mmol, 72% recovered), (ii) cyclopentadiene dimer (trace), and (iii) a mixture (0.46 g, 1.0 mmol, 100%) of the *cis*- and *trans*-criss-cross 2 : 1 adducts (Xa and b) in the ratio 1 : 5.

Attempted Pyrolysis of 1,2,3,6-Tetrahydro-4,5-dimethyl-2,2-bis(trifluoromethyl)-1-(2,2,2-trifluoro-1-trifluoromethyl-

ethylideneamino)pyridine (VIII). The adduct (0.41 g, 1.0 mmol), passed at low pressure (*ca.* 1 mmHg) through a Pyrex tube heated at 350 °C (30 min), gave only unchanged adduct (0.41 g, 1.0 mmol, 100% recovered).

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