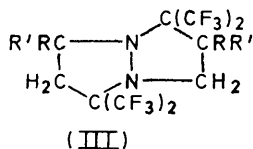
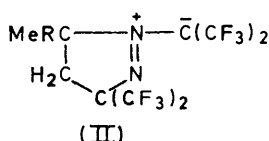
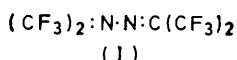


Unsaturated Nitrogen Compounds containing Fluorine. Part VI.¹ Reactions of Hexafluoroacetone Azine with 2-Methylbut-2-ene, 2,3-Dimethylbut-2-ene, 2,3-Dimethylbut-1-ene, and Cyclopentene²

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The thermal reaction of hexafluoroacetone azine with 2-methylbut-2-ene gives nitrogen, 1,1,1,3,3,3-hexafluoropropane, a mixture (32%) of eight bis(trifluoromethyl)carbene-olefin adducts including the alkene $(\text{CF}_3)_2\text{C}:\text{CH}\cdot\text{CHMeEt}$ (7%) and the cyclopropane $(\text{CF}_3)_2\text{C}:\text{CMe}_2\cdot\text{CHMe}$ (13%), and tar. In contrast the reaction with 2,3-dimethylbut-2-ene gives mainly the 1 : 1 adduct $(\text{CF}_3)_2\text{C}:\text{N}\cdot\text{NH}\cdot\text{C}(\text{CF}_3)_2\cdot\text{CH}_2\cdot\text{CMe}:\text{CMe}_2$, but nitrogen, 1,1,1,3,3,3-hexafluoropropane, and the carbene-olefin adducts $(\text{CF}_3)_2\text{C}:\text{CH}\cdot\text{CHMe}\cdot\text{CHMe}_2$ (2%), $(\text{CF}_3)_2\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHMe}_2$ (7%), and $(\text{CF}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CMe}:\text{CMe}_2$ (15%) are also formed; the reaction with 2,3-dimethylbut-1-ene gives the same products, together with the cyclopropane $(\text{CF}_3)_2\text{C}:\text{CH}_2\cdot\text{CMe}\cdot\text{CHMe}_2$, and the recovered olefin fraction from both reactions contained the but-2-ene and the but-1-ene in the ratio *ca.* 4 : 1. The reaction with cyclopentene gives the Δ^3 -pyrazoline $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}:\text{C}(\text{CF}_3)_2\cdot\text{NH}\cdot\text{N}\cdot\text{CH}(\text{CF}_3)_2$ (63%), together with nitrogen, 1,1,1,3,3,3-hexafluoropropane, and the carbene-olefin adducts $(\text{CF}_3)_2\text{CH}\cdot\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2$ and $(\text{CF}_3)_2\text{C}:\text{C}[\text{CH}_2]_3\cdot\text{CH}_2$.

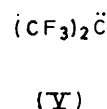
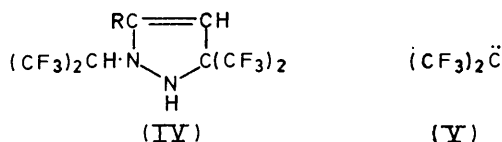
It has been reported^{3,4} that hexafluoroacetone azine (I) reacts in the temperature range 20–70 °C with olefins of the type $\text{H}_2\text{C}:\text{CMeR}$ ($\text{R} = \text{Me}, \text{Et}, \text{or Pr}^i$) to give stable



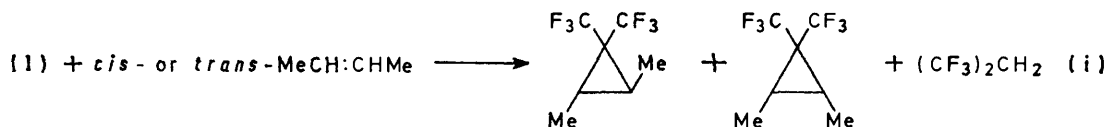
azomethinimines (II) which are precursors of the 'criss-cross' 2 : 1 adducts (III).

With olefins of the type $\text{H}_2\text{C}:\text{CHR}$ ($\text{R} = \text{H}, \text{Me}, \text{or Et}$)

olefins $\text{H}_2\text{C}:\text{CHR}$ ($\text{R} = \text{Pr}^i$ or Bu^t) react with the azine (I) at *ca.* 100 °C to afford the Δ^3 -pyrazolines (IV), possibly *via* rearrangement of intermediate azomethinimines.³ It has also been observed that 1,3-dienes react with the azine (I) to give 1 : 1 and 2 : 1 adducts.¹



In contrast cyclohexene and *cis*- or *trans*-but-2-ene react with the azine (I) at *ca.* 190 °C to afford products formally derived from bis(trifluoromethyl)carbene (V)⁶ [reaction (i)]. The reaction of the azine with isobutene



the exclusive products are the criss-cross adducts (III); $\text{R} = \text{H}, \text{R}' = \text{H}, \text{Me}, \text{or Et}$)^{3,5} and even in the presence of an excess of azine (I) the suspected azomethinimine intermediates have not been detected.³ However, the

¹ Part V, S. E. Armstrong and A. E. Tipping, *J.C.S. Perkin I*, 1975, 1411.

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

³ S. E. Armstrong and A. E. Tipping, *J.C.S. Perkin I*, 1975, 538.

at 160 °C also gives products which include the carbene-olefin adduct $(\text{CF}_3)_2\text{C}:\text{CH}\cdot\text{CHMe}_2$ (16%).³

⁴ 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.

⁵ T. P. Forshaw and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 2404.

⁶ T. P. Forshaw and A. E. Tipping, *J.C.S. Perkin I*, 1972, 1059.

In the present work the thermal reactions of the azine (I) with cyclopentene, allyl chloride, 2-methylbut-2-ene, and 2,3-dimethylbut-2-ene have been carried out; the results obtained from this last reaction prompted an investigation of the reaction of the azine with 2,3-dimethylbut-1-ene under comparable conditions. The conditions employed and the identified products obtained are shown in the Table.

reaction of cyclopentadiene with the azine (I) reacted quantitatively with cyclopentadiene to afford a criss-cross adduct.¹ The other products, nitrogen and (V)—(VII), are considered to arise by a radical mechanism similar to that postulated⁶ previously to explain the products from the reaction of the azine (I) with cyclohexene or the but-2-enes, *i.e.* formation of the radical $(CF_3)_2\dot{C}H$ and the diradical (XVIII) (Scheme 1).

Reactions of hexafluoroacetone azine with olefins

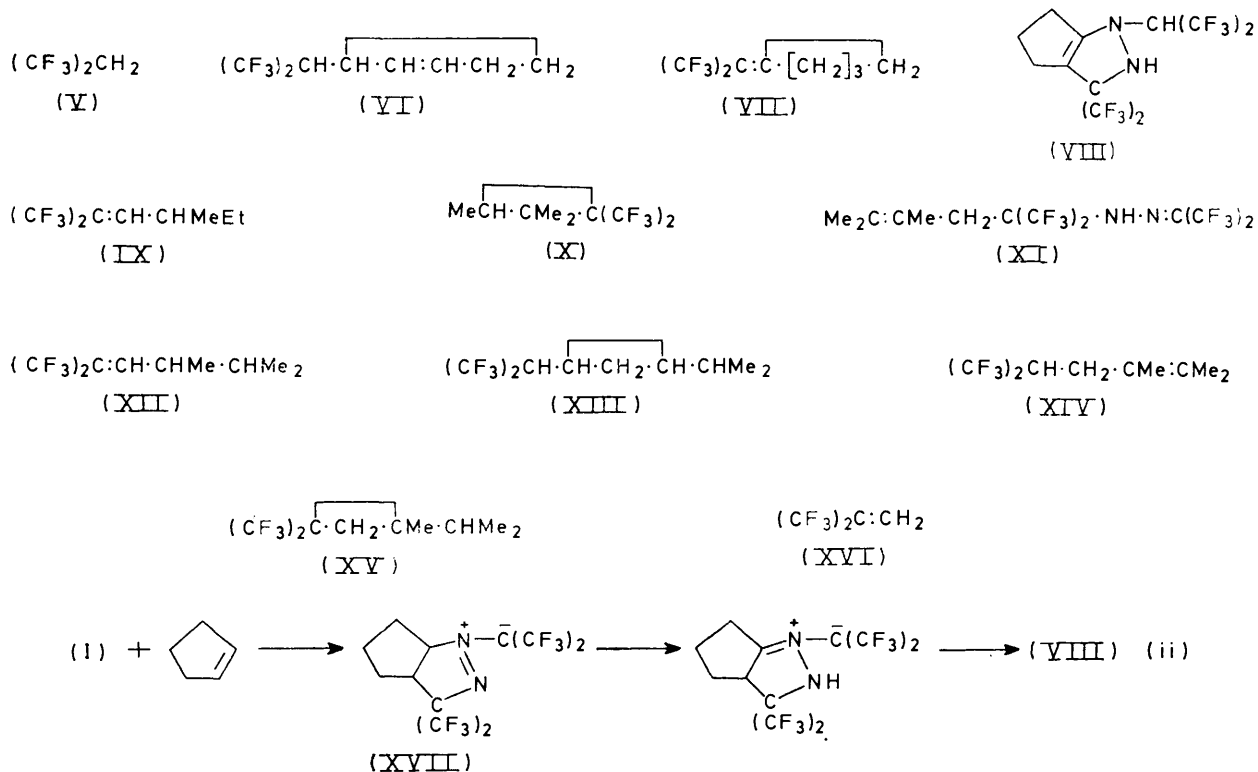
Olefin	Azine : olefin ratio	Temp. (°C)	Time (h)	Recovered reactants (%)		Products (%)			
				Azine	Olefin	N ₂	(V)	Others	
$CH_2 \cdot (CH_2)_2 \cdot CH \cdot CH$	1 : 3	140	48					(VI) 4; (VII) 3; (VIII) 63 *	
$MeHC : CMe_2$	1 : 2.9	170	24	23	59	16	6	(IX) 7; (X) 13 †	
$Me_2C : CMe_2$	1 : 3	160	24		69	53	3	(XI) 43; (XII) 2; (XIII) 7;	
					39 ‡	38	7	(XIV) 15	
$H_2C : CMe \cdot CHMe_2$	1 : 2	170	45		8 §	51	6	(XI) 16; (XII) 15; (XIII) 7;	
$H_2C : CH \cdot CH_2Cl$	1 : 2	170	30		18	27		(XIV) 7; (XV) 4	
								(XVI) 63	

All the reactions also gave considerable amounts of tar.

* An unidentified carbene-olefin adduct, $C_8H_8F_6$ (1%), and two unidentified higher-boiling compounds (*ca.* 8%) were also formed. † A mixture of six unidentified carbene-olefin adducts, $C_8H_{10}F_4$ (12%), was also formed. ‡ 2,3-Dimethylbut-1-ene (10%) was also obtained. § 2,3-Dimethylbut-2-ene (33%) was also obtained. || A complex high-boiling fraction (*ca.* 15%) was also formed.

The major product from the cyclopentene reaction, the Δ^3 -pyrazoline (VIII), is possibly formed *via* rearrangement of the azomethinimine (XVII) arising from 1,3-dipolar addition of azine (I) to the olefin [reaction (ii)].

It is possible that the unidentified carbene adduct has structure (XIX), that of the expected product from rearrangement of the diradical (XVIII). This reaction thus contrasts with the corresponding cyclohexene



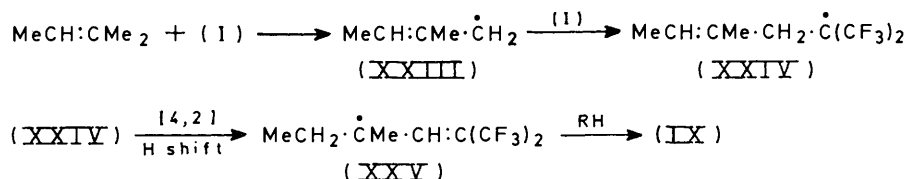
However, if the propanide (XVII) is formed as an intermediate, it is surprising that it did not also react to some extent with the excess of olefin to give the corresponding criss-cross adduct; the propanide isolated from the

reaction⁶ which, although carried out at higher temperature (180 °C), gave only nitrogen, (V), carbene-olefin adducts, and a complex higher-boiling mixture.

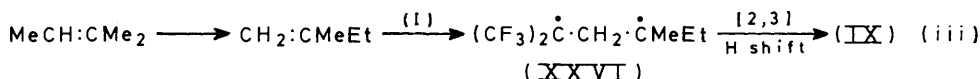
The reaction of the azine (I) with 2-methylbut-2-ene

This is considered to be less likely, however, because the rearranged olefin was not detected in the recovered olefin fraction and other products which were formed from the reaction of 2-methylbut-1-ene with the azine (I)³ were not observed.

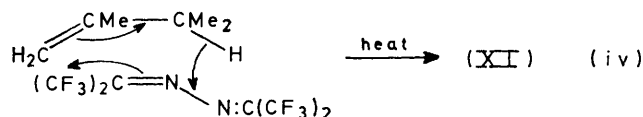
The recovered olefin fractions from the reactions of the



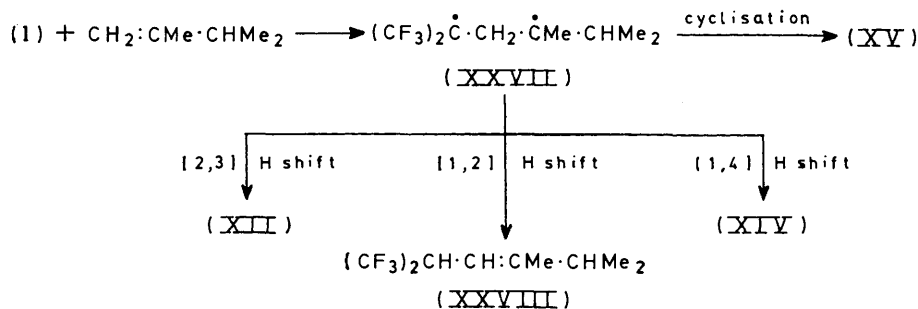
SCHEME 3



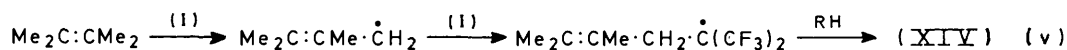
azine (I) with 2,3-dimethylbut-2-ene and 2,3-dimethylbut-1-ene both contained the but-2-ene and the but-1-ene in the ratio *ca.* 4:1. The two reactions gave the same products, except for the cyclopropane (XV) isolated from the but-1-ene reaction, but the product yield from the but-1-ene reaction (55%) carried out at 170 °C was lower than that obtained from the but-2-ene reaction (74%) carried out at 160 °C. Both reactions gave the 1:1 adduct (XI) as the major product and this compound



is considered to be formed by the 'ene' reaction involving the but-1-ene [reaction (iv)]. Compounds (XII) and (XV) and possibly (XIV) are also considered to be formed from the but-1-ene *via* the diradical (XXVII) (Scheme 4).



SCHEME 4



The other possible rearrangement product of the diradical (XXVII), the alkene (XXVIII), was not detected in the products, consistent with previous observations that rearrangement of diradicals of type $(\text{CF}_3)_2\dot{\text{C}}\cdot\text{CHR}\cdot\dot{\text{C}}\text{R}'\text{R}''$ gives olefins of the type $(\text{CF}_3)_2\text{C}:\text{CR}\cdot\text{CHR}'\text{R}''$ in preference to those of the type $(\text{CF}_3)_2\dot{\text{C}}\text{H}\cdot\text{CR}'\text{R}''$.^{3,6}

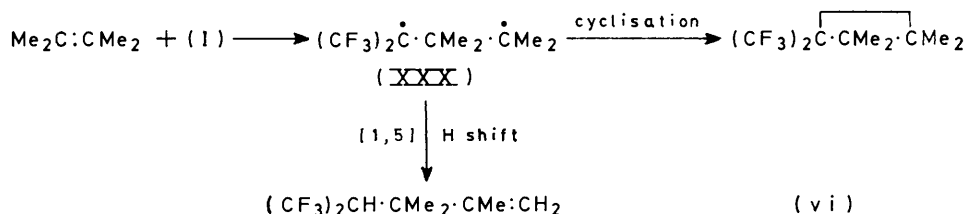
Since the alkene (XIV) is formed in appreciably higher yield in the but-2-ene than in the but-1-ene reaction it may be formed mainly *via* attack of the allyl radical (XXIX) on the azine (I) [reaction (v)]. The remaining product, the cyclopropane (XIII), was tentatively identified on the basis of the following spectral evidence: (i)

absence of i.r. absorption in the C:C region; (ii) ¹H n.m.r. absorptions at 3.92 (1 H, sept, *J* 8.3 and 3.5 Hz), 4.9–5.3 (5 H, complex), and 5.85 (6 H, overlapping dd) p.p.m. to high field of external benzene and ¹⁹F absorption at δ –9.50 p.p.m. (complex m) the region expected for a $(\text{CF}_3)_2\text{CH}$ group. The low field absorption (*τ ca.* 7) was assigned to $(\text{CF}_3)_2\text{CH}\cdot\text{CH}<$; *cf.* $(\text{CF}_3)_2\text{CH}\cdot\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2$ (VI), *τ* 7.07 (sepd, *J*_{F,F} 9.0, *J*_{F,H} 3.0 Hz). The high-field absorption (dd at *τ ca.* 8.9) is as expected for non-equivalent methyls in an isopropyl group. The remaining complex absorption at 4.9–5.3 p.p.m. is assigned to the five cyclopropane ring protons. Finally (iii), a base peak at *m/e* 43 (CHMe_2^+) in the mass spectrum indicated the presence of a CHMe_2 group. It is not at present apparent how the cyclopropane (XIII) is formed.

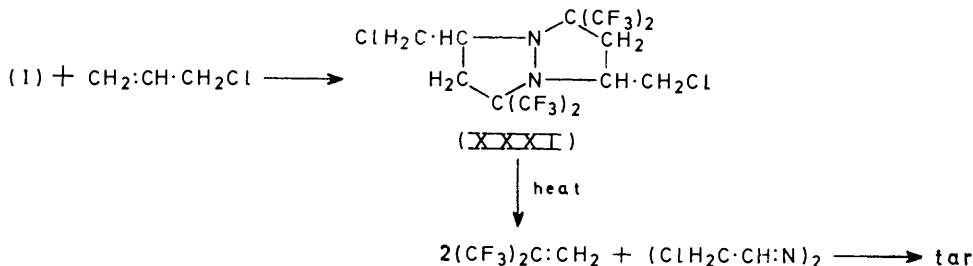
It is noteworthy that products derived from the expected diradical intermediate (XXX) were not detected [reaction (vi)].

The reaction of 2,3-dimethylbut-1-ene with the azine (I) at lower temperature (70 °C) gives the propanide (II; R = Et) (96%),³ but this compound was not detected in the products from the present reaction. It was also found that isomerisation of the but-2-ene or the but-1-ene did not occur to any marked extent when they were heated

alone under the reaction conditions; the olefin isomerisations must thus involve interaction either with the azine (I) or with other species formed during the reactions.



The reaction of the azine (I) with allyl chloride at 170 °C gave nitrogen and the alkene (XVI) as the only identified products. The alkene (XVI) is obtained in >80% yield when the alk-1-ene criss-cross adducts (III; R = H, R' = H, Me, Et, etc.) are pyrolysed at ca. 200 °C,⁵ and it is probable that the olefin is produced in the present reaction by decomposition of the initially formed criss-cross adduct (XXXI). This indicates that the chlorine-containing criss-cross adduct is of lower thermal stability than those derived from the alk-1-enes.



EXPERIMENTAL

All the reactions were carried out *in vacuo* in Pyrex tubes (ca. 300 cm³) and the g.l.c. columns used for product separation are described in the text; other techniques used are as described previously.^{1,3}

Hexafluoroacetone azine (I) was prepared by treatment of the corresponding imine with potassium fluoride and bromine,⁷ followed by photolysis of the resultant *N*-bromoimine.⁸ The olefins were commercial samples which, where necessary, were purified before use.

N.m.r. and mass spectral data for new compounds are available as Supplementary Publication No. SUP 21458 (8 pp.).†

Reactions of Hexafluoroacetone Azine with Alkenes.—(a) *With 2-methylbut-2-ene.* A mixture of the azine (4.92 g, 15.0 mmol) and the alkene (3.08 g, 44.0 mmol), heated at 170 °C (24 h), gave (i) nitrogen (0.17 g, 6.15 mmol, 53%; *M*, 28), (ii) 1,1,1,3,3,3-hexafluoropropane (V) (0.09 g, 0.6 mmol, 3%), (iii) unchanged 2-methylbut-2-ene (2.12 g, 30.3 mmol, 69% recovered), (iv) unchanged azine (1.12 g, 3.4 mmol, 23% recovered), (v) a higher-boiling liquid fraction (1.60 g) (Found: *M*, 220. Calc. for C₈H₁₀F₆: *M*, 220), and (vi) a viscous tar (2.87 g), which did not yield any volatile material on attempted low-pressure distillation and was not examined further. The higher-boiling fraction was shown by g.l.c. (4 m Silicone MS 550 oil at 70 °C) to contain eight components from which only the two major components (ratio 9 : 15)

could be separated. The minor component was identified as 1,1,1-trifluoro-4-methyl-2-(trifluoromethyl)hex-2-ene (IX) (0.37 g, 1.68 mmol, 7%) (Found: C, 43.4; H, 4.7%; *M*, 221.

C₈H₁₀F₆ requires C, 43.6; H, 4.6%; *M*, 220), b.p. (Siwoloboff) 100 °C; λ_{max}, 5.95s μm (C:C str.); and the major component as 1,1,2-trimethyl-3,3-bis(trifluoromethyl)cyclopropane (X) (0.65 g, 2.95 mmol, 13%) (Found: C, 43.4; H, 4.7%; *M*, 220), b.p. (Siwoloboff) 110 °C.

(b) *With 2,3-dimethylbut-2-ene.* A mixture of the azine (3.28 g, 10.0 mmol) and the alkene (2.52 g, 30.0 mmol), sealed *in vacuo* in a Pyrex tube (ca. 300 cm³) and heated at 160 °C (24 h), gave (i) nitrogen (0.11 g, 3.76 mmol, 38%; *M*, 28), (ii) 1,1,1,3,3,3-hexafluoropropane (V) (0.22 g, 1.44 mmol, 7%), (iii) a mixture (1.24 g, 14.8 mmol) (Found: *M*,

84. Calc. for C₈H₁₂: *M*, 84), shown by g.l.c. (2 m MS 550 oil at 50 °C) and i.r. and n.m.r. spectroscopy to consist of unchanged 2,3-dimethylbut-2-ene (0.99 g, 11.8 mmol, 39% recovered) and 2,3-dimethylbut-1-ene (0.25 g, 3.0 mmol, 10%), (iv) a higher-boiling volatile fraction (1.10 g, 4.70 mmol) shown by g.l.c. (7 m Kel-F 40 oil at 90 °C) to consist of three components (A—C) in the ratio 1 : 4 : 9, and (v) a residue (3.11 g), which was fractionated at ca. 3 mmHg to give a distillate (2.11 g) and a viscous tarry residue (1.0 g); the distillate, which contained one major component (ca. 70%) and ten minor components (g.l.c. on 2 m Kel-F 90 oil at 120 °C) was redistilled to afford the pure major component, 1,1,1-trifluoro-7,8-dimethyl-2,5,5-tris(trifluoromethyl)-3,4-diazanona-2,7-diene (XI) (1.75 g, 4.25 mmol, 43%) (Found: C, 35.2; H, 2.8; N, 6.6%; *M*⁺, 412. C₁₂H₁₂F₁₂N₂ requires C, 35.0; H, 2.9; N, 6.8%; *M*, 412), b.p. (Siwoloboff) 183 °C at 740 mmHg; λ_{max}, 3.03 m (NH str.) and 6.18s μm (C:C or C:N str.).

The components A—C were separated by g.l.c. (as before) to give (i) 1,1,1-trifluoro-4,5-dimethyl-2-trifluoromethylhex-2-ene (XII) (0.08 g, 0.34 mmol, 2%) (Found: C, 46.0; H, 5.4%; *M*, 233. C₉H₁₂F₆ requires C, 46.2; H, 5.1%; *M*, 234), b.p. (Siwoloboff) 118 °C at 744 mmHg; λ_{max}, 5.95s μm (C:C str.) (ii) 1-isopropyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)cyclopropane (XIII) (0.31 g, 1.33 mmol, 7%) (Found: C, 46.0; H, 5.1%; *M*, 235), b.p. (Siwoloboff) 123 °C at 744 mmHg; and (iii) 6,6,6-trifluoro-2,3-dimethyl-5-trifluoro-

⁷ T. K. Ruff, *J. Org. Chem.*, 1967, **32**, 1675.

⁸ W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, 1965, **30**, 1398.

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

methylhex-2-ene (XIV) (0.17 g, 3.03 mmol, 15%) (Found: C, 46.5; H, 5.3%; *M*, 235), b.p. (Siwoloboff) 129 °C at 742 mmHg.

(c) *With 2,3-dimethylbut-1-ene*. A mixture of the azine (4.92 g, 15.0 mmol) and the alkene (2.52 g, 30.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 300 cm³) and heated at 170 °C (45 h), gave (i) nitrogen (0.21 g, 7.6 mmol, 51%), (ii) 1,1,1,3,3,3-hexafluoropropane (V) (0.26 g, 1.73 mmol, 6%), (iii) a mixture (1.04 g, 12.38 mmol, 41%; *M*, 84), which was shown as in the previous experiment to contain unchanged 2,3-dimethylbut-1-ene (0.20 g, 2.38 mmol, 8% recovered) and 2,3-dimethylbut-2-ene (0.84 g, 10.0 mmol, 33%), (iv) a higher-boiling fraction (2.26 g, 9.7 mmol) which was shown by g.l.c. (7 m Kel-F oil at 90 °C) to contain components A–C as in the previous experiment and a new component D in the ratio 16 : 7 : 7 : 4, and (v) a residue (3.65 g), which on low-pressure distillation (*ca.* 3 mmHg) gave a viscous tar (2.15 g) and a distillate (1.50 g); the distillate was shown by g.l.c. (2 m Kel-F 90 oil at 120 °C) to contain numerous (>10) minor components and a major component, separated and identified, as in the previous experiment, as the 1 : 1 adduct (XI) (0.95 g, 2.3 mmol, 16%). Component D was separated from the higher-boiling fraction by g.l.c. (7 m Kel-F 40 oil at 90 °C) to give 1-isopropyl-1-methyl-2,2-bis-(trifluoromethyl)cyclopropane (XV) (0.26 g, 1.12 mmol, 4%) (Found: C, 46.1; H, 5.2%; *M*, 235. C₉H₁₂F₆ requires C, 46.2; H, 5.1%; *M*, 234), b.p. (Siwoloboff) 127 °C at 742 mmHg; the fraction also contained 1,1,1-trifluoro-4,5-dimethyl-2-trifluoromethylhex-2-ene (XII) (1.08 g, 4.62 mmol, 15%), 1-isopropyl-2-(2,2,2-trifluoro-1-trifluoromethylethyl)cyclopropane (XIII) (0.46 g, 1.97 mmol, 7%), and 6,6,6-trifluoro-2,3-dimethyl-5-trifluoromethylhex-2-ene (XIV) (0.46 g, 1.97 mmol, 7%).

(d) *With cyclopentene*. A mixture of the azine (4.92 g, 15.0 mmol) and cyclopentene (3.06 g, 45.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 300 cm³) and heated at 140 °C (48 h), gave (i) nitrogen (0.066 g, 2.37 mmol, 16%; *M*, 28),

(ii) 1,1,1,3,3,3-hexafluoropropane (V) (0.28 g, 1.83 mmol, 6%) (Found: *M*, 151. Calc. for C₃H₂F₆: *M*, 152), (iii) unchanged cyclopentene (1.80 g, 26.5 mmol, 59% recovered), (iv) a higher-boiling volatile fraction (0.48 g), and (v) a residue (5.33 g).

The higher-boiling fraction was shown by g.l.c. (2 m MS 550 oil at 60 °C) to contain three components in the ratio 4 : 1 : 3 and the two major components were separated by g.l.c. (4 m Silicone SE 30 oil at 100 °C) to give 3-(2,2,2-trifluoro-1-trifluoromethylethyl)cyclopentene (VI) (0.23 g, 1.05 mmol, 4%) (Found: C, 44.1; H, 4.0%; *M*, 218. C₈H₈F₆ requires C, 44.4; H, 3.7%; *M*, 218), b.p. (Siwoloboff) 116 °C; and (2,2,2-trifluoro-1-trifluoromethylethylidene)cyclopentane (VII) (0.18 g, 0.82 mmol, 3%) (Found: C, 44.1; H, 3.8%; *M*, 218), b.p. (Siwoloboff) 136 °C; λ_{max} 5.99s μm (C:C str.), respectively.

The residue was fractionated at *ca.* 5 mmHg to yield a distillate (4.13 g) and a viscous tar (1.20 g), and the distillate was shown by g.l.c. (2 m Apiezon M at 120 °C) to contain three components in the ratio 3 : 42 : 2. The major component was purified by redistillation at low-pressure to give 1,2,3,4,5,6-hexahydro-3,3-bis(trifluoromethyl)-1-(2,2,2-trifluoro-1-trifluoromethylethyl)cyclopentapyrazole (VIII) (3.72 g, 9.40 mmol, 63%) (Found: C, 33.5; H, 2.3; N, 6.9%; *M*⁺, 396. C₁₁H₈F₁₂N₂ requires C, 33.4; H, 2.0; N, 7.0%; *M*, 396), b.p. (Siwoloboff) 189 °C; λ_{max} 5.88s μm (C:C str.).

(e) *With allyl chloride*. A mixture of the azine (3.94 g, 12.0 mmol) and allyl chloride (1.84 g, 24.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 300 cm³) and heated at 170 °C (30 h), gave (i) nitrogen (0.09 g, 3.23 mmol, 27%), (ii) 3,3,3-trifluoro-2-trifluoromethylpropene (XVI) (2.46 g, 15.0 mmol, 63%), (iii) unchanged allyl chloride (0.32 g, 4.2 mmol, 18% recovered), (iv) a higher-boiling volatile fraction (0.50 g) shown by g.l.c. (2 m Carbowax at 90 °C) to contain eight components and not examined further, and (v) a viscous tar (2.40 g).

[5/516 Received, 17th March, 1975]