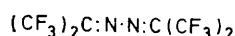2716

Unsaturated Nitrogen Compounds containing Fluorine. Part III.[1] Reactions of Hexafluoroacetone Azine with Alkanes, Cycloalkanes, and Trimethylsilane
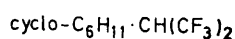
By **Stuart E. Armstrong** and **Anthony E. Tipping,*** Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Hexafluoroacetone azine reacts with cyclopentane at 140 °C to give nitrogen, 1,1,1,3,3,3-hexafluoropropane, (2,2,2-trifluoro-1-trifluoromethylethyl)cyclopentane, 2-(cyclopentylazo)-1,1,1,3,3,3-hexafluoropropane, 4,4a,5,-6,7,7a-hexahydro-3,4,4-tris(trifluoromethyl)-1H-cyclopenta[c]pyridazine, and tar; at higher temperatures the azo-compound is not present. The corresponding reactions with cyclobutane, cycloheptane, 2-methylpropane, 2-methylbutane, 2-methylpentane, and trimethylsilane are also reported. The major products from the last reaction are hexafluoroacetone (2,2,2-trifluoro-1-trifluoromethylethyl)hydrazone and N-trimethylsilylhexafluoro-isopropylideneamine in the ratio ca. 1 : 2.
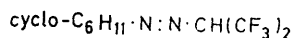
HEXAFLUOROACETONE AZINE (I) has been found [1,2] to react with acetylene and hydrocarbon olefins under thermal or photochemical conditions to give criss-cross 2 : 1 adducts and/or products formally derived from the intermediacy of bis(trifluoromethyl)carbene. Later
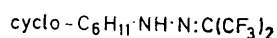
$(CF_3)_2C:N\cdot N:C(CF_3)_2$

(I)

$cyclo\text{-}C_6H_{11}\cdot CH(CF_3)_2$

(II)

$cyclo\text{-}C_6H_{11}\cdot N:N\cdot CH(CF_3)_2$

(III)

$cyclo\text{-}C_6H_{11}\cdot NH\cdot N:C(CF_3)_2$

(IV)

work has shown that in certain cases 1 : 1 olefin–azine adducts are also formed.[3] It has also been reported [4,5] that the azine (I) reacts with cyclohexane at 129—170 °C in the presence or absence of benzene to give nitrogen, the
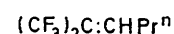
thermal conditions are now reported. The conditions used and the products obtained from the alkane reactions are shown in the Table.
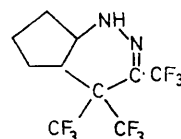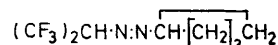
$(CF_3)_2CH_2$ $(CF_3)_2CHR$ $(CF_3)_2C:CHPr^n$

(V)   (VI)   (VII)

(VIII)

$(CF_3)_2CH\cdot N:N\cdot CH\text{-}[CH_2]_3CH_2$
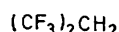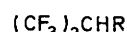
(IX)

1,1,1,3,3,3-Hexafluoropropane (V) was identified by comparison of its n.m.r. spectra with those obtained

Reactions of hexafluoroacetone azine with alkanes

R in alkane RH	Molar ratio (alkane : azine)	Temp. (°C)	Time (h)	Recovered reactants (%)		Products (%) *					
				Alkane	Azine	N₂	(V)	(VI)	(VII)	(VIII)	(IX)
cyclo-C₄H₇	2	170	72	67		63	21	2	3		†
cyclo-C₅H₉	2	170	12	39		53	21	28			
cyclo-C₅H₉	1 ‡	160	36	33	33	48	20	23		15	
cyclo-C₅H₉	8	140	24	88		31	17	28		12	11
cyclo-C₅H₉	0·75	155	30		13	30	24	16		13	
cyclo-C₇H₁₃	1	150 170	40 50 }	31	38	40	26				†
cyclo-C₇H₁₃	2 §	180	30	72		50	21				†
Me₃C	2	200	70	60	9	83	15	29			†
EtMe₂C	2	200	70	87	28	75	25				†
PrⁿMe₂C	2	200 250	70 150 }	83		60	ca. 20				†

* Based on azine consumed; all reactions also gave considerable amounts of tar. † Small amounts of multicomponent high-boiling liquids also formed. ‡ Benzene (1 mol. equiv.) also present. § Benzene (2 mol. equiv.) also present.

substituted cycloalkane (II) (36—71%), the azo-compound (III) (11—17%), the hydrazone (IV) (3—18%), and unidentified material (14—32%), in relative yields depending on the conditions. A radical double-chain mechanism was proposed.[5]

The reactions of the azine (I) with cyclobutane, cyclopentane, cycloheptane, 2-methylpropane, 2-methylbutane, 2-methylpentane, and trimethylsilane, under

previously [6] and the structures of the other products were established by a consideration of their i.r., mass, and n.m.r. spectra.

The formation of the insertion products (VI) and the azo-compound (IX) can be interpreted by the unique double-chain mechanism put forward to explain the products from the thermal reaction of the azine (I) with cyclohexane [5] (Scheme 1). The radical R· necessary to

[1] Part II, T. P. Forshaw and A. E. Tipping, J.C.S. Perkin I, 1972, 1059.

[2] T. P. Forshaw and A. E. Tipping, J. Chem. Soc. (C), 1971, 2404.

[3] S. E. Armstrong and A. E. Tipping, J. Fluorine Chem., 1973, 3, 119.

[4] W. J. Middleton, D. M. Gale, and C. G. Krespan, J. Amer. Chem. Soc., 1968, 90, 6813.

[5] W. J. Middleton, J. Amer. Chem. Soc., 1971, 93, 423.

[6] D. D. Elleman, L. C. Brown, and D. Williams, J. Mol. Spectroscopy, 1961, 7, 393; R. N. Haszeldine, J. R. McAllister, and A. E. Tipping, unpublished results.

initiate these chain reactions was considered to arise *via* reaction of the imine $(CF_3)_2C:N\cdot$ radical with the alkane RH. This imine radical is probably present in equilibrium concentration when the azine (I) is heated since the
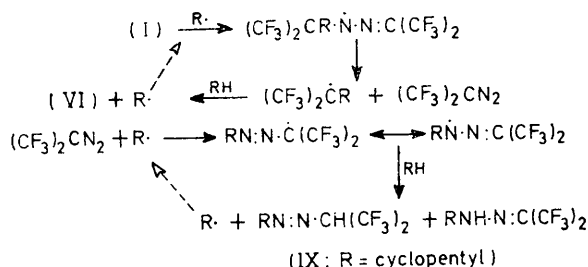
SCHEME 1

azine initiates the polymerisation of acrylonitrile at 95 °C.[5] The pyrolysis products of the azine [7] also suggest that the azine first dissociates into imine radicals [equation (i)]. The propane (V) was not reported as a product from the reactions of azine (I) with cyclohexane,[4,5]

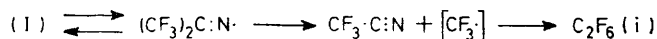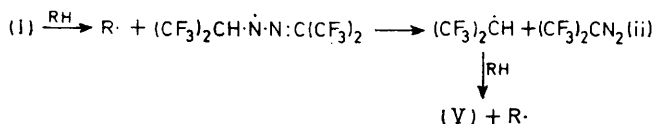$$(I) \; \rightleftarrows \; (CF_3)_2C:N\cdot \; \longrightarrow \; CF_3\cdot C:N + \left[CF_3\cdot \right] \; \longrightarrow \; C_2F_6 \; (i)$$

but if the reaction tubes were vented to remove nitrogen before work-up of the higher-boiling products the propane (V) could well have remained undetected. In a qualitative experiment carried out by us using a 2 : 1 molar ratio of cyclohexane to azine (I) at 170 °C (12 h), the propane (V) (*ca.* 20%) was found among the products.

The radical double-chain mechanism does not account for the formation of the propane (V), a relatively major product (15—26%). However, a mechanism has been put forward previously [1] to account for the formation of this compound (8—18%) in the reactions of the azine (I) with *cis*- and *trans*-but-2-ene and cyclohexene, and it is considered that the propane is probably formed similarly in the present work [equation (ii)]. This mechanism also

$$(I) \xrightarrow{RH} R\cdot + (CF_3)_2CH\cdot N:N:C(CF_3)_2 \longrightarrow (CF_3)_2\dot{C}H + (CF_3)_2CN_2 \text{(ii)}$$

$$\downarrow RH$$

$$(Y) + R\cdot$$

provides an alternative route for the formation of the alkyl or cycloalkyl (R·) radical required as the initiating species in the double-chain mechanism. It is therefore considered probable that both mechanisms are operating in the reactions of the azine (I) with alkanes and cycloalkanes.

In the reaction of cyclohexane with the azine (I) carried out in benzene a low yield (4%) of the carbene–benzene adduct, 1,1-bis(trifluoromethyl)norcaradiene was isolated,[5] in contrast to the high yield (*ca.* 60%) obtained when the diazoalkane $(CF_3)_2CN_2$ is pyrolysed in benzene.[8] In the present work the norcaradiene was not detected in the products from the reactions of the azine (I) with cyclopentane or cyclohexane carried out in the presence

of benzene. It is therefore probable that decomposition of the diazoalkane intermediate $(CF_3)_2CN_2$ to give nitrogen and the carbene $(CF_3)_2\ddot{C}$ is only a minor reaction pathway and that the diazoalkane reacts further to give products which, under the reaction conditions, decompose to form nitrogen and the tar observed.

The yields of insertion products of type (VI) vary in the order cyclohexane > cyclopentane > cyclobutane, and the minimum temperature at which reaction could be initiated follows the order cyclobutane > cyclopentane > cyclohexane. The most probable explanation for these observations is that the C–H bond strengths follow the order cyclobutane > cyclopentane > cyclohexane, which is the order of ring strain in the cycloalkanes.

It is suggested that the temperatures required to initiate the reactions are, in general, too high to favour the formation of hydrazones [RNH·N:C(CF_3)_2] or azo-compounds [RN:N·CH(CF_3)_2]. In this respect it is significant that the azo-compound (IX) is only observed in the cyclopentane reaction carried out at the lowest temperature (140 °C) and that the yield of the hydrazone (IV) is reported [5] to decrease significantly as the temperature is increased (129 °C, 18%; 170 °C, 3%).

We cannot at present explain the low yields or absence of the insertion compounds of type (VI) in certain of the reactions.

The ring-opened product (VII) (3%) formed in the cyclobutane reaction probably arises *via* initial cyclobutyl radical attack on the azine (I) followed by ring-opening and hydrogen abstraction (Scheme 2).
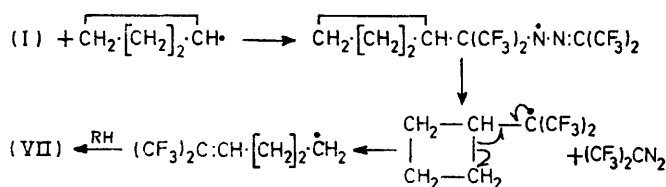
SCHEME 2

The pyridazine (VIII) is probably formed *via* further reaction of the insertion product (VI, R = cyclopentyl) (Scheme 3).
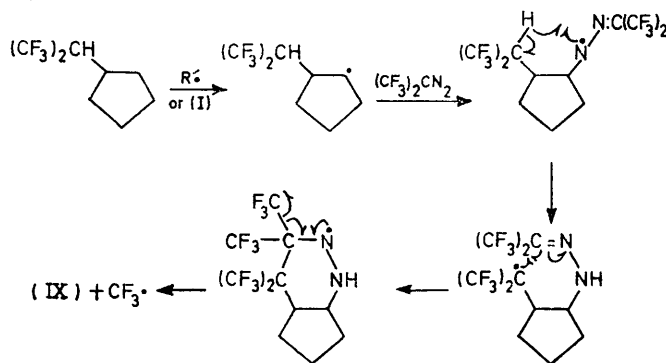
SCHEME 3

The reaction of the azine (I) with trimethylsilane (1 : 2 molar ratio) at 180 °C gave nitrogen (6%), (V) (5%), unchanged trimethylsilane (41% recovered), a high-boiling

[7] T. P. Forshaw and A. E. Tipping, *Chem. Comm.*, 1969, 816.
[8] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1966, **88**, 3617.

liquid consisting of hexafluoroacetone (2,2,2-trifluoro-1-trifluoromethylethyl)hydrazone (X) (38%), N-trimethyl-silylhexafluoroisopropylideneamine (XI) (35%), dimethyl-(3,3,3-trifluoro-2-trifluoromethylpropyl)silane (XII) (5%), trimethyl-(2,2,2-trifluoro-1-trifluoromethylethyl)silane (XIII) (1%), and three minor unidentified

$$(CF_3)_2C:N\cdot NH\cdot CH(CF_3)_2 \qquad (CF_3)_2C:N\cdot SiMe_3$$

$$(X) \qquad\qquad (XI)$$

$$(CF_3)_2CH\cdot CH_2\cdot SiHMe_2 \qquad (CF_3)_2CH\cdot SiMe_3$$

$$(XII) \qquad\qquad (XIII)$$

components, and a small amount of tar. The structures of the products were established on the basis of their i.r., n.m.r., and mass spectra. Compound (XI) was previously identified as a product from the reaction of N-lithiohexafluoroisopropylideneamine with chloro(trimethyl)silane.[9]

The initiation steps (iii)—(v) are possibly involved in the reaction. The first mechanism (iii) is considered unlikely because the imine $(CF_3)_2C:NH$ was not detected in

$$(I) \rightleftharpoons (CF_3)_2C:N\cdot \xrightarrow{HSiMe_3} (CF_3)_2C:NH + Me_3Si\cdot \qquad (iii)$$

$$(I) + HSiMe_3 \longrightarrow (CF_3)_2CH\cdot \dot{N}\cdot N:C(CF_3)_2 + Me_3Si\cdot \qquad (iv)$$

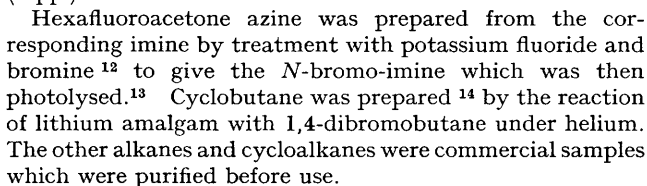$$(CF_3)_2C=N\cdot N:C(CF_3)_2$$
$$\quad H\text{—}SiMe_3 \longrightarrow (CF_3)_2CH\cdot N(SiMe_3)\cdot N:C(CF_3)_2 \qquad (v)$$

$$(XIV)$$

the reaction products. Although step (v) cannot be discounted, step (iv) is considered more likely because further reactions of the radicals so formed can account for

$$(CF_3)_2CH\cdot\dot{N}\cdot N:C(CF_3)_2 \longrightarrow (CF_3)_2\dot{C}H + (CF_3)_2CN_2$$
$$\qquad\qquad \downarrow HSiMe_3 \qquad\qquad \downarrow HSiMe_3$$
$$\qquad Me_3Si\cdot + (V) \qquad N_2 + (XII) + (XIII)$$

$$(I) + Me_3Si\cdot \longrightarrow (CF_3)_2\dot{C}\cdot N(SiMe_3)\cdot N:C(CF_3)_2 \xrightarrow{HSiMe_3} (XIV)$$

$$(XV)$$

$$\underset{\text{heat}}{\longrightarrow} (X) + 2(XI)$$

SCHEME 4

the isolated products (Scheme 4). Trimethylsilyl radical attack on the azine (I) takes place at nitrogen to give the radical (XV) and not at carbon (contrast alkyl and cyclo-

alkyl radical attack) to give the alternative radical, $Me_3Si\cdot C(CF_3)_2\cdot\dot{N}\cdot N:C(CF_3)_2$, presumably because the N–Si bond (ca. 104 kcal mol⁻¹)[10] is considerably stronger than the C–Si bond (ca. 76 kcal mol⁻¹).[10] The products (X) and (XI) were isolated in the ratio 1 : 1·84, which is close to the ratio 1 : 2 required by Scheme 4.

It is unlikely that the carbene insertion products (XII) and (XIII) (ratio 5 : 1) are formed by direct $(CF_3)_2\ddot{C}$ insertion into a C–H and the Si–H bond of trimethylsilane, respectively, since it has been observed that the carbene $CHF_2\cdot\ddot{C}F$ inserts exclusively into the Si–H bond of trimethylsilane.[11]
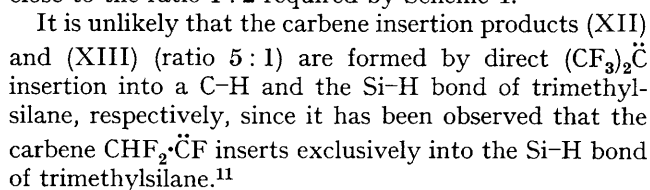
EXPERIMENTAL

Reactants and products were manipulated where possible in a conventional vacuum system to avoid contamination with air or moisture. Reactions were carried out in vacuo in Pyrex tubes (ca. 300 cm³ unless stated otherwise). Volatile products were separated by fractional condensation in vacuo followed by preparative g.l.c. (Pye 104 or Perkin-Elmer F21 instrument; columns as indicated in the text). Products which were non-volatile at room temperature were purified by sublimation under reduced pressure. Nitrogen, the only volatile product which was non-condensible at −196 °C, was absorbed at −196 °C in vacuo on activated charcoal. The charcoal was then desorbed thermally and the nitrogen identified by absence of i.r. absorption and by molecular weight determination. The identities of products were established by i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer with sodium chloride optics), molecular weight (Regnault's method), n.m.r. spectroscopy (Perkin-Elmer R10 or R20 spectrometer operating at 56·46 MHz for ¹⁹F or 60·0 MHz for ¹H or a Varian HA 100 instrument operating at 94·1 MHz for ¹⁹F or 100·0 MHz for ¹H and with external trifluoroacetic acid and internal tetramethylsilane as the respective references), and mass spectrometry (A.E.I. MS/2H or MS/902 spectrometer). N.m.r. and/or mass spectral data for compounds marked with an asterisk are available in Supplementary Publication No. SUP 21158 (4 pp.).*

Hexafluoroacetone azine was prepared from the corresponding imine by treatment with potassium fluoride and bromine[12] to give the N-bromo-imine which was then photolysed.[13] Cyclobutane was prepared[14] by the reaction of lithium amalgam with 1,4-dibromobutane under helium. The other alkanes and cycloalkanes were commercial samples which were purified before use.

Reactions of Hexafluoroacetone Azine.—(a) *With 2-methylpropane.* A mixture of the azine (4·92 g, 15·0 mmol) and the alkane (1·75 g, 30·0 mmol), heated at 200 °C (70 h), gave (i) nitrogen (0·32 g, 11·3 mmol, 83%) (Found: M, 29. Calc. for N_2: M, 28), (ii) a mixture (1·65 g, 22·0 mmol), shown by i.r. and n.m.r. spectroscopy and g.l.c. (4 m Silicone MS 550 oil at 25 °C) to consist of unchanged 2-methylpropane (1·04 g, 18·0 mmol, 60% recovered) and 1,1,1,3,3,3-hexafluoropropane (0·61 g, 4·0 mmol, 15%), (iii) unchanged azine (0·46 g, 1·4 mmol, 9% recovered), (iv) a higher-boiling mixture (2·02 g) of one major and five minor components from which

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

[9] T. P. Forshaw and A. E. Tipping, unpublished results.

[10] T. L. Cottrell, 'The Strengths of Chemical Bonds,' 2nd edn., Butterworths, London, 1958.

[11] R. N. Haszeldine, A. E. Tipping, and R. O'B. Watts, *Chem. Comm.*, 1969, 1364.

[12] J. K. Ruff, *J. Org. Chem.*, 1967, **32**, 1675.

[13] W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, 1965, **30**, 1398.

[14] D. S. Connor, *Tetrahedron Letters*, 1967, **49**, 4925.

the major component was separated by g.l.c. (4 m column at 80 °C) and identified as 1,1,1-*trifluoro-3,3-dimethyl-2-(trifluoromethyl)butane* * (1·65 g, 7·94 mmol, 29% based on azine, 66% based on alkane) (Found: C, 40·4; H, 5·1; F, 54·2%; *M*, 207. $C_7H_{10}F_6$ requires C, 40·4; H, 4·9; F, 54·7%; *M*, 208), b.p. (Siwoloboff) 89 °C; and (v) a brown non-volatile tar (2·21 g).

(b) *With 2-methylbutane.* A mixture of the azine (4·92 g, 15·0 mmol) and the alkane (2·20 g, 30·0 mmol), heated at 200 °C (70 h), gave (i) nitrogen (0·23 g, 8·04 mmol, 75%), (ii) 1,1,1,3,3,3-hexafluoropropane (0·82 g, 5·4 mmol, 25%) (Found: *M*, 151. Calc. for $C_3H_2F_6$: *M*, 152), (iii) unchanged 2-methylbutane (1·87 g, 26·0 mmol, 87% recovered), (iv) unchanged azine (1·4 g, 4·2 mmol, 28% recovered), (v) a liquid higher-boiling mixture (0·50 g), which was shown by g.l.c. (2 m column at 70 °C) to consist of five components in approximately equal amounts, and (vi) a brown non-volatile tar (2·28 g).

(c) *With 2-methylpentane.* A mixture of the azine (4·92 g, 15·0 mmol) and the alkane (2·60 g, 30·0 mmol), heated at 200 °C (70 h) and then at 250 °C (50 h), gave (i) nitrogen (0·25 g, 9·0 mmol, 60%), (ii) a mixture (1·30 g, 12·4 mmol; *M*, 105) shown by i.r. spectroscopy and g.l.c. (4 m Kel-F 10 oil at 0 °C) to consist mainly of 1,1,1,3,3,3-hexafluoropropane and trifluoromethane, together with small amounts of trifluoroacetonitrile and silicon tetrafluoride, (iii) unchanged 2-methylpentane (2·18 g, 25·0 mmol, 83% recovered), (iv) a higher-boiling mixture (0·5 g) shown by g.l.c. (2 m Silicone MS 550 oil at 80 °C) to contain ten components none of which was major, and (v) a carbonaceous tar (3·24 g).

(d) *With cyclobutane.* A mixture of the azine (3·94 g, 12·0 mmol) and the cycloalkane (1·34 g, 24·0 mmol), heated at 170 °C (72 h), gave (i) nitrogen (0·21 g, 7·5 mmol, 63%), (ii) a mixture (1·66 g, 21·0 mmol) shown by i.r. spectroscopy and g.l.c. (4 m Kel-F 10 oil at 28 °C) to consist of unchanged cyclobutane (0·90 g, 16·0 mmol, 67% recovered) and 1,1,1,-3,3,3-hexafluoropropane (0·76 g, 5·0 mmol, 21%), (iii) a higher-boiling fraction (0·30 g), shown by g.l.c. (4 m Kel-F 10 oil at 70 °C) to consist of two major components (ratio 8 : 5) and ten minor components, and (iv) a brown non-volatile tar (3·10 g).

The two major components of the higher-boiling mixture were separated by g.l.c. (as above) and identified as 1,1,1-*trifluoro-2-trifluoromethylhex-2-ene* * (0·16 g, 0·78 mmol, 3% based on azine, 10% based on cyclobutane) (Found: C, 40·9; H, 4·1%; *M*, 207. $C_7H_8F_6$ requires C, 40·8; H, 3·9%; *M*, 206), b.p. (Siwoloboff) 92 °C, $\lambda_{max.}$ 5·96s μm (C:C str.) and (2,2,2-*trifluoro-1-trifluoromethylethyl)cyclobutane* * (0·10 g, 0·49 mmol, 2% based on azine, 6% based on cyclobutane) (Found: C, 41·0; H, 4·1%; *M*, 206. $C_7H_8F_6$ requires C, 40·8; H, 3·9%; *M*, 206), b.p. (Siwoloboff) 98 °C.

(e) *With cyclopentane at* 170 °C. A mixture of the azine (4·92 g, 15·0 mmol) and cyclopentane (2·1 g, 30·0 mmol), heated at 170 °C (12 h), gave (i) nitrogen (0·22 g, 7·9 mmol, 53%); (ii) 1,1,1,3,3,3-hexafluoropropane (0·97 g, 6·4 mmol, 21%); (iii) unchanged cyclopentane (0·81 g, 11·6 mmol, 39% recovered); (iv) a higher-boiling fraction which was identified as (2,2,2-*trifluoro-1-trifluoromethylethyl)cyclopentane* * (1·83 g, 8·3 mmol, 28% based on azine, 45% based on cyclopentane) (Found: C, 43·9; H, 4·6%; *M*, 219. $C_8H_{10}F_6$ requires C, 43·6; H, 4·6%; *M*, 220), b.p. (Siwoloboff) 122 °C; and (v) a dark brown non-volatile solid residue (3·17 g) which did not contain any crystalline material.

(f) *With cyclopentane in the presence of benzene.* A mixture of the azine (4·92 g, 15·0 mmol), cyclopentane (1·05 g,

15·0 mmol), and benzene (1·17 g, 15·0 mmol), heated at 160 °C (36 h), gave (i) nitrogen (0·13 g, 4·8 mmol, 48%), (ii) 1,1,1,3,3,3-hexafluoropropane (0·61 g, 4·0 mmol, 20%), (iii) a mixture (3·13 g, 24·5 mmol) shown by i.r. spectroscopy and g.l.c. (4 m Silicone MS 550 oil at 80 °C) to consist of unchanged benzene (1·13 g, 14·5 mmol, 97% recovered), unchanged cyclopentane (0·35 g, 5·0 mmol, 33% recovered), and unchanged azine (1·65 g, 5·0 mmol, 33% recovered), (iv) (2,2,2-trifluoro-1-trifluoromethylethyl)cyclopentane (1·0 g, 4·6 mmol, 23% based on azine, 46% based on cyclopentane), and (v) a brown non-volatile residue (2·25 g) which was washed from the reaction tube with hot carbon tetrachloride. The solvent was removed *in vacuo*, and the residue sublimed *in vacuo* to give a non-volatile brown tar (1·71 g) and a white solid identified as 4,4a,5,6,7,7a-*hexahydro-3,4,4-tris(trifluoromethyl)-1H-cyclopenta*[c]*pyridazine* (VIII) * (0·50 g, 1·52 mmol, 15% based on azine or cyclopentane) (Found: C, 36·7; H, 3·1; N, 8·6%; *M*+, 328. $C_{10}H_9F_9N_2$ requires C, 36·6; H, 2·8; N, 8·6%; *M*, 328), m.p. 140—141 °C, $\lambda_{max.}$ 3·06m (NH str.), 6·08m (C:N str.), and 6·43 μm (NH bend).

(g) *With cyclopentane at* 155 °C. A mixture of the azine (5·45 g, 16·6 mmol) and cyclopentane (0·84 g, 12·0 mmol), heated at 155 °C (30 h), gave (i) nitrogen (0·12 g, 4·40 mmol, 30%), (ii) 1,1,1,3,3,3-hexafluoropropane (1·07 g, 7·05 mmol, 24%), (iii) unchanged azine (0·70 g, 2·1 mmol, 13% recovered), (iv) (2,2,2-trifluoro-1-trifluoromethylethyl)cyclopentane (1·0 g, 4·55 mmol, 16% based on azine, 38% based on cyclopentane), and (v) involatile material (3·43 g) which was worked up as in the previous experiment to give the pyridazine (0·60 g, 1·83 mmol, 13% based on azine, 15% based on cyclopentane) and a brown tar (2·80 g).

(h) *With cyclopentane at* 140 °C. A mixture of the azine (1·64 g, 5·0 mmol) and cyclopentane (2·80 g, 40·0 mmol), heated at 140 °C (24 h), gave (i) nitrogen (0·04 g, 1·55 mmol, 31%), (ii) 1,1,1,3,3,3-hexafluoropropane (0·26 g, 1·71 mmol, 17%), (iii) unchanged cyclopentane (2·45 g, 35·0 mmol, 88% recovered), (iv) a higher-boiling fraction (0·75 g), which was separated by g.l.c. (4 m Kel-F 10 oil at 70 °C) into its two components identified as (2,2,2-trifluoro-1-trifluoromethylethyl)cyclopentane (0·61 g, 2·8 mmol, 28% based on azine, 56% based on cyclopentane) and 2-(*cyclopentylazo)-*1,1,1,3,3,3-*hexafluoropropane* (IX) * (0·14 g, 0·56 mmol, 11% based on azine or cyclopentane) (Found: C, 38·9; H, 3·7; N, 11·1%; *M*, 247. $C_8H_{10}F_6N_2$ requires C, 38·7; H, 4·0; N, 11·3%; *M*, 248), b.p. (Siwoloboff) 133 °C at 740 mmHg, $\lambda_{max.}$ 6·43m μm (N:N str.), and (v) a residue (0·84 g), which was worked up as in experiment (f) to give the pyridazine (0·20 g, 0·61 mmol, 12% based on azine or cyclopentane) and a brown tar (0·62 g).

(j) *With cycloheptane.* A mixture of the azine (5·25 g, 16·0 mmol) and cycloheptane (1·57 g, 16·0 mmol), heated at 150 °C (40 h) and then at 170 °C (50 h), gave (i) nitrogen (0·14 g, 5·04 mmol, 50%), (ii) 1,1,1,3,3,3-hexafluoropropane (0·79 g, 5·2 mmol, 26%), (iii) unchanged azine (2·0 g, 6·1 mmol, 38% recovered), (iv) unchanged cycloheptane (0·50 g, 5·0 mmol, 31% recovered), (v) a compound (0·01 g) tentatively identified as (2,2,2-trifluoro-1-trifluoromethylethyl)cycloheptane, ^{19}F n.m.r. δ −15·4 p.p.m. [d, $(CF_3)_2CH$, J_{H,CF_3} 9·0 Hz], and (vi) a residue (3·4 g), which was washed from the reaction tube with diethyl ether. The ether was removed *in vacuo* and the residue distilled under reduced pressure to give a mobile liquid (1·0 g), g.l.c. (2 m Apiezon M at 50 °C) of which showed the presence of *ca.* ten components, and a brown tar (2·3 g).

(k) *With cycloheptane in the presence of benzene.* A mixture of the azine (1·64 g, 5·0 mmol), cycloheptane (0·98 g, 10·0 mmol), and benzene (0·88 g, 11·3 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 100 cm³) and heated at 180 °C (30 h), gave (i) nitrogen (0·06 g, 2·0 mmol, 40%), (ii) 1,1,1,3,3,3-hexafluoropropane (0·33 g, 2·11 mmol, 21%), (iii) a mixture (1·37 g, 18·24 mmol), which was shown by i.r. spectroscopy and g.l.c. (4 m Silicone MS 550 oil at 80 °C) to consist of unchanged benzene (0·86 g, 11·0 mmol, 98% recovered) and unchanged cycloheptane (0·71 g, 7·24 mmol, 72% recovered), (iv) a higher-boiling liquid (trace), and (v) a brown tar (1·51 g).

(l) *With trimethylsilane.* A mixture of the azine (2·95 g, 9·0 mmol) and trimethylsilane (1·33 g, 18·0 mmol), heated at 180 °C (72 g), gave (i) nitrogen (0·02 g, 0·55 mmol, 6%), (ii) a mixture (0·69 g, 8·3 mmol) shown by i.r. spectroscopy and g.l.c. (4 m Kel-F 10 oil at 30 °C) to consist of 1,1,1,3,3,3-hexafluoropropane (0·14 g, 0·92 mmol, 5%) and unchanged trimethylsilane (0·55 g, 7·38 mmol, 41% recovered), (iii) a higher-boiling fraction (3·35 g) which was shown by g.l.c. (2 m Apiezon M at 60 °C) to contain two major components (ratio 8 : 15) and seven minor components, and (iv) a non-volatile residue (0·2 g).

The two major components and two of the minor components of the higher-boiling fraction (iii) were separated by g.l.c. (4 m Silicone MS 550 oil at 85 °C) and were identified as *hexafluoroacetone* (2,2,2-*trifluoro*-1-*trifluoromethylethyl*)-*hydrazone* (X) * (1·11 g, 3·4 mmol, 38%) (Found: C, 22·0; H, 0·9; N, 8·2%; M^+, 330. $C_6H_2F_{12}N_2$ requires C, 21·8; H, 0·7; N, 8·5%; M, 330), b.p. (Siwoloboff) 89 °C; $\lambda_{max.}$ 2·95 (NH str.) and 6·13 (C⋮N str.) μm; N-*trimethylsilylhexa-fluoroisopropylideneamine* (XI) * (1·48 g, 6·2 mmol, 35% based on azine, 58% based on silane) (Found: C, 30·3; H, 4·1; F, 48·1; N, 6·1%; M^+, 237. $C_6H_9F_6NSi$ requires C, 30·4; H, 3·8; F, 48·1; N, 5·9%; M, 237), b.p. (Siwoloboff) 89 °C; $\lambda_{max.}$ 5·63 μm (C⋮N str.); dimethyl-(3,3,3-trifluoro-2-trifluoromethylpropyl)silane (XII) * (0·20 g, 0·87 mmol, 5% based on azine, 8% based on silane); and trimethyl-(2,2,2-trifluoro-1-trifluoromethylethyl)silane (XIII) * (0·05 g, 0·23 mmol, 1% based on azine, 2% based on silane).