1099. *Polyfluorocycloalkenes. Part II.*[1]* *Reaction of Decafluorocyclohexene with Ammonia and with Isopropylamine.*

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Decafluorocyclohexene reacts with ammonia and with isopropylamine in ether to give 1-aminoheptafluoro-3-iminocyclohex-1-ene and the isopropyl analogue, respectively. Both compounds are susceptible to acid hydrolysis giving 1-amino- and 1-isopropylamino-heptafluorocyclohex-1-en-3-one, respectively. More drastic hydrolysis of the former compound affords heptafluoro-1-hydroxycyclohex-1-en-3-one. Raney nickel in ethanol converts 1-aminoheptafluoro-3-iminocyclohexene into tetrafluoro-*m*-phenylenediamine.

Perfluoro-olefins are known to react vigorously with ammonia and amines[2-4] and an addition-elimination reaction path has been suggested.[3] Decafluorocyclohexene followed

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[1] Part I, D. R. Sayers, R. Stephens, and J. C. Tatlow, *J.*, 1964, 3035.

[2] R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, *J. Amer. Chem. Soc.*, 1950, **72**, 3646.

[3] C. O. Parker, *J. Amer. Chem. Soc.*, 1959, **81**, 2183.

[4] T. Mill, J. O. Rodin, R. M. Silverstein, and C. Woolf, *J. Org. Chem.*, 1963, **28**, 836.

the same pattern of behaviour with ammonia and with isopropylamine to give conjugated amino-imines (IX) and (X), respectively (vinylogous amidines). The exact sequence of elimination is not clear. Either an α-elimination process such as that depicted [*e.g.*, (II) → (IV)] is possible or a β-elimination [*e.g.*, (II) → (III)], but the same final products, (IX) and (X), arise from both. From each reaction, in fact, the appropriate amino-imine was the only product which was found. Undecafluorocyclohexane gave the same two compounds, (IX) and (X), in excellent yield, obviously *via* preliminary dehydrofluorination to decafluorocyclohexene (I).

The presence of a conjugated system in the amino-imines (IX) and (X) was clearly indicated by selective absorption in the ultraviolet region, very similar to that given by the analogous 1-amino-2-chlorotetrafluoro-3-iminocyclopentane,[3] tautomers of the type (VIII) clearly being unfavoured. Absorption maxima in the infrared spectra occurred at frequencies consistent with the main structural features of these compounds (Table). Oxidation of both amino-imines (IX) and (X) with potassium permanganate gave hexafluoroglutaric acid, which confirmed the presence, in each, of three adjacent $-CF_2-$ groups. Acetylation of 1-amino-heptafluoro-3-iminocyclohex-1-ene (IX) gave a diacetyl compound probably carrying an acetyl on each nitrogen atom (cf. acylation of perfluoro-amidines[5]) and retaining a conjugated system. The diacetyl derivative was not hydrolysed under mild conditions, but on being heated with methanol or ethanol, gave alcohol-addition products devoid of selective absorption in the ultraviolet region. It is probable that addition occurred across the double bond of the C=N group, the alkoxide ion attacking the carbon atom.

Attempted hydrogenation with a nickel catalyst of the amino-imine (IX) gave 2,4,5,6-tetrafluoro-1,3-phenylenediamine (XV) characterised as the bis(trifluoroacetyl) compound. The orientation was confirmed by fluorine-19 n.m.r. spectroscopy, the spectrum showing three magnetically different kinds of fluorine atom in the molecule in the intensity ratio of 1:2:1 (the *ortho* and *para*-isomers show two peaks and a single peak, respectively). This aromatic diamine has also been prepared by the ammoniation of pentafluoroaniline.[6] The aromatisation process presumably involves a repetitive sequence of hydrogen addition and dehydrofluorination by nickel, and the yield of tetrafluoro-*m*-phenylenediamine was substantially increased by the addition of an alkaline resin and the use of ethanol as solvent. An unsuccessful attempt was made to confirm the allocated structure by a synthesis based on *m*-xylene.[7] The latter was converted into perfluoro-1,3-dimethylcyclohexane with cobaltic fluoride, and this defluorinated to decafluoro-*m*-xylene which was hydrolysed to tetrafluoroisophthalic acid. The azide of this was prepared from the acid chloride, but it decomposed to give an intractable solid, presumably a polymer.

Both amino-imines (IX) and (X) were readily hydrolysed with dilute mineral acid to highly crystalline amino-ketones (XI) and (XII). Neither of these compounds displayed chemical properties characteristic of the carbonyl or amino-group, in accord with their being vinylogous acid amides. Oxidation of the isopropylamino-ketone (XII) with permanganate gave hexafluoroglutaric acid. The presence of a conjugated system was confirmed by strong absorption in the ultraviolet. Infrared spectroscopy provided quite good evidence for the amino-ketone structure; absorptions attributable to the principal features of the system were observed (Table). Proton n.m.r. measurements of 2M-solutions of 1-amino-3-iminoheptafluorocyclohex-1-ene (IX), 1-amino-heptafluorocyclohexen-3-one (XI), 1-isopropylamino-heptafluorocyclohexen-3-one (XII), and trifluoroacetamide in acetone revealed broad singlets in the region 6·8 to 7·5 p.p.m. downfield from tetramethylsilane, in the approximate intensity ratio of 3:2:1:2, respectively, in agreement with vinylogous acid amide structures for (XI) and (XII) in this solvent; the presence of the tautomeric zwitterion-type system (XIV) is possible and may be reflected in the high crystallinity and solubility characteristics of (XI) and (XII).

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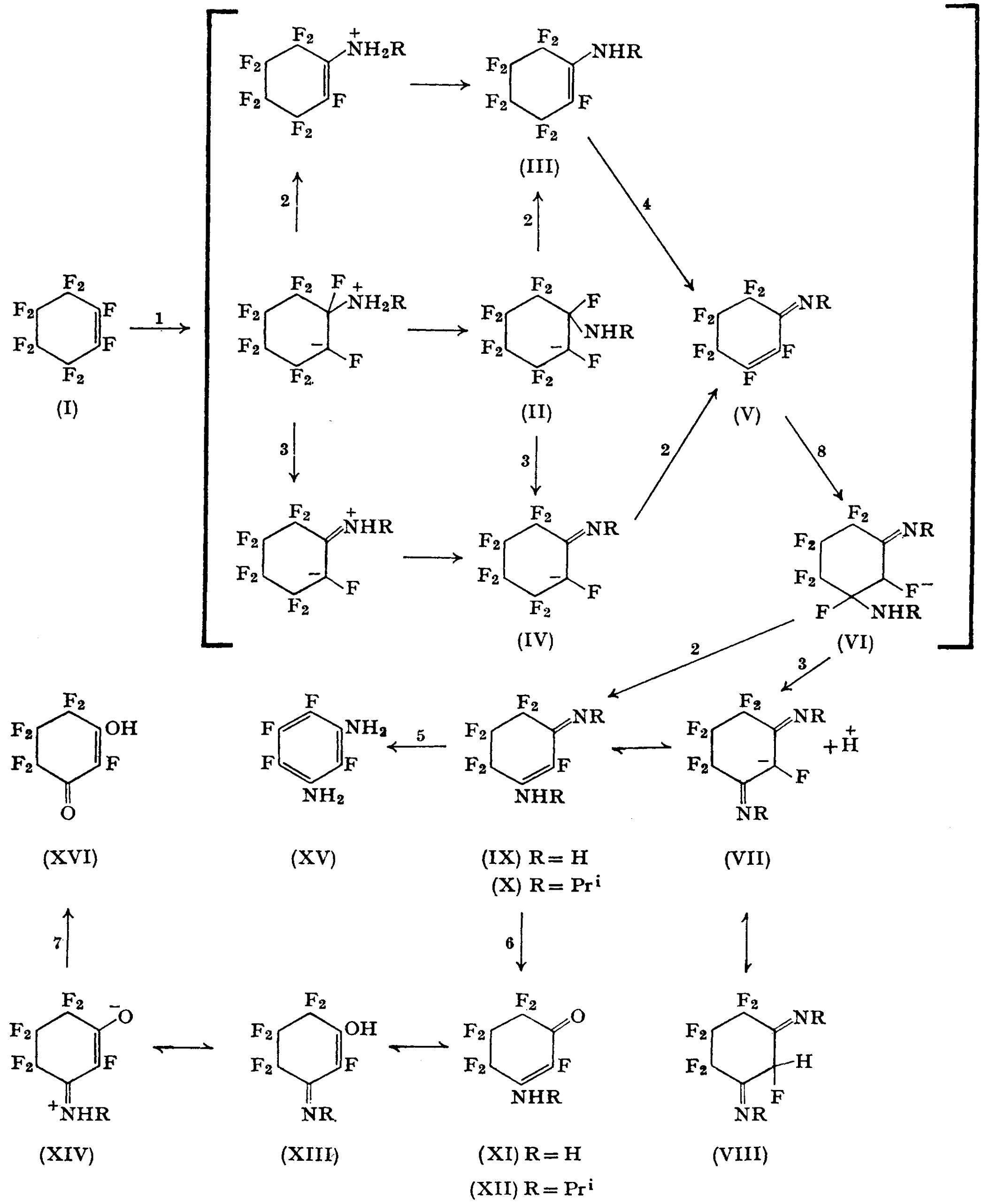
[5] W. L. Reilly and H. C. Brown, *J. Amer. Chem. Soc.*, 1956, **78**, 6032.

[6] G. M. Brooke, J. Burdon, M. Stacey, and J. C. Tatlow, *J.*, 1960, 1768.

[7] B. Gething, C. R. Patrick, and J. C. Tatlow, *J.*, 1961, 1574.

An alternative structure, (XIII), containing a hydroxyl group, for the compounds (XI) and (XII) would be expected to undergo ready hydrolysis to the hydroxy-ketone system (XVI), whereas this conversion required prolonged treatment with hydrochloric acid at 100°. The product of hydrolysis of 1-aminoheptafluorocyclohexen-3-one (XI) was an extremely hygroscopic liquid devoid of ketonic carbonyl properties, but sufficiently acidic to be



Reagents: 1, RNH_2; 2, loss of F^- (β); 3, loss of F^- (α); 4, loss of HF (1,4); 5, Raney nickel–amberlite resin in ethanol; 6, dilute mineral acid at 15°; 7, dilute mineral acid at 100°; 8, RNH_2, possible pathways as before.

Compound	$\nu_{max.}$ (cm.$^{-1}$)[a]			$\lambda_{max.}$ (Å)[b]	
	>C=O	>N–H	>C=C<	λ	ε (× 10^4)
1-Aminoheptafluoro-3-iminocyclohexene (IX)	[t]	1615	1665	2910	2·75
Heptafluoro-1-isopropylamino-3-isopropyliminocyclohexene (X)[c]	[t]	1525 1631	1647 1663	3055	2·6
Hexafluoro-1-amino-3-imino-2-trifluoromethylcyclohexene[8]	[t]	1625	1665	2750	0·55
1-Aminoheptafluorocyclohexen-3-one (XI)	1710	1630	1660	3010	2·8
Heptafluoro-1-isopropylaminocyclohexen-3-one (XII)	1695	1550	1663	3130	3·17
Hexafluoro-1-amino-2-trifluoromethylcyclohexen-3-one[8]	1710	1600	1670	2800	3·07
Trifluoroacetamide	1750	1625	[t]	—	—
Heptafluoro-1-hydroxycyclohexen-3-one hydrate	1730		1685	2960	2·95

[a] 0·1-mm. thick films of 0·2M-solutions in diethyl ether. [b] Solutions in ethanol. [c] Liquid film. [t] Transparent.

titrated, the perfluoro-vinylogous acid structure presumably being favoured over the β-diketone. It displayed the expected infrared and ultraviolet absorption spectra (Table).

EXPERIMENTAL

Reaction of Decafluorocyclohexene with Ammonia.—A slow stream of ammonia was passed for 3½ hr. through a solution of the olefin (10·9 g.) in ether (110 c.c.); a yellow colour developed, and much solid was deposited. Water was added and the ether layer combined with the ether extracts of the aqueous phase, dried ($MgSO_4$), filtered, and evaporated to leave a solid which was sublimed and then recrystallised from carbon tetrachloride to give 1-*aminoheptafluoro*-3-*iminocyclohexene* (7·0 g.), m. p. 95—96° (Found: C, 30·5; H, 1·5; N, 11·8; F, 56·1. $C_6H_3F_7N_2$ requires C, 30·5; H, 1·3; N, 11·9; F, 56·3%).

Reaction of Undecafluorocyclohexane with Ammonia.—Undecafluorocyclohexane (66·0 g.) in ether (1 l.) was treated with ammonia in the above way for 6 hr. Isolation as before gave 1-amino-2,4,4,5,5,6,6-heptafluoro-3-iminocyclohexene (47·6 g.), m. p. 96° (Found: C, 30·4; H, 1·3%).

The amino-imine (2·0 g.), acetic acid (2·5 c.c.), and acetic anhydride (2·5 c.c.) were refluxed for 1 hr. and then poured into water to give the suspected 1-*acetamido*-3-*acetimido*-2,4,4,5,5,6,6-*heptafluorocyclohexene* (2·8 g.), m. p. 126° (from aqueous ethanol) (Found: C, 37·8; H, 2·3; F, 41·5. $C_{10}H_7F_7N_2O_2$ requires C, 37·5; H, 2·2; F, 41·6%); $\nu_{max.}$ 3290 (>NH) and 1726 cm.$^{-1}$ (>C=O) (several absorptions in the range 1695—1500 cm.$^{-1}$ could not be unambiguously assigned); $\lambda_{max.}$ 2850 Å (ε, 1·11 × 10^4) in ethanol. When this compound (28·5 g.) was refluxed with ethanol (100 c.c.) for ½ hr. and water added, a precipitate (10·0 g.,) m. p. 186—188°, was obtained which was recrystallised from aqueous ethanol to give an *ethanol adduct* (3·0 g.), m. p. 192° (Found: C, 39·7; H, 3·1; F, 36·4; ethoxyl, 12·2. $C_{12}H_{13}F_7N_2O_3$ requires C, 39·3; H, 3·5; F, 36·3; ethoxyl 12·3%); there was no selective absorption in the range 2200—3500 Å. When the first-mentioned diacetyl compound was treated with methanol in the same way it gave a *methanol adduct*, m. p. 190° (Found: C, 37·9; H, 3·3; F, 37·3; MeO, 9·1. $C_{11}H_{11}F_7N_2O_3$ requires C, 37·5; H, 3·1; F, 37·8; MeO, 8·8%), with i.r. spectrum different from that of the ethanol adduct. Again there was no selective absorption in the range 2200—3500 Å.

Oxidation of 1-*Aminoheptafluoro*-3-*iminocyclohexene.*—This compound (1·13 g.), potassium permanganate (15·0 g.), and water (50 c.c.) were kept in a rocking autoclave at 90—120° for 18 hr. The usual isolation procedure gave hexafluoroglutaric acid which was characterised as its dianilinium salt (1·16 g.), m. p. 218—220° (Found: C, 47·8; H, 3·7; F, 26·7%; Equiv., 212. Calc. for $C_{17}H_{16}F_6N_2O_4$: C, 47·9; H, 3·8; F, 26·8%; Equiv., 213), and as its bis-*S*-benzylthiouronium salt, m. p. 189—190° (Found: C, 44·4; H, 4·0. Calc. for $C_{21}H_{22}F_6N_4O_4S_2$: C, 44·1; H, 3·9%).

Hydrolysis of 1-*Aminoheptafluoro*-3-*iminocyclohexene.*—This compound (6·3 g.) and 2N-hydrochloric acid (200 c.c.) were kept at 15° for 2 hr. The precipitate (4·6 g.) was recrystallised from

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[8] P. Carter, C. R. Patrick, and J. C. Tatlow, unpublished work.

carbon tetrachloride to give 1-*aminoheptafluorocyclohexen*-3-*one* (3·6 g.), m. p. 100° [Found: C, 30·7; H, 0·7; F, 55·8%; *M* (cryoscopically in benzene), 245. $C_6H_2F_7NO$ requires C, 30·4; H, 0·8; F, 56·1%; *M*, 237].

The amino-ketone (2·58 g.) was suspended in 2N-hydrochloric acid (80 c.c.) at 100° for 48 hr; 16N-hydrochloric acid (30 c.c.) was then added and the mixture extracted with ether for 48 hr. The dried ($MgSO_4$), filtered extract was evaporated and the residue (2·8 g.) distilled to give the extremely hygroscopic hydrated *heptafluoro*-1-*hydroxycyclohexen*-3-*one* (0·95 g.), b. p. 60—70°/4 mm., $n_D^{19\cdot5}$ 1·3990 (Found: C, 27·8; H, 1·2%; Equiv., 260. $C_6HF_7O_2,H_2O$ requires C, 28·1; H, 1·2%; Equiv., 256).

2,4,4,5,5,6,6-*Heptafluoro*-1-*isopropylamino*-3-*isopropyliminocyclohexene*.—Isopropylamine (5 c.c.) was added to decafluorocyclohexene (5·0 g.) in ether (30 c.c.); heat was evolved and a solid precipitated. After ½ hr., water was added, the ether layer separated, washed, dried ($MgSO_4$), filtered, and evaporated to leave a liquid which was distilled *in vacuo* to give 2,4,4,5,5,6,6-*heptafluoro*-1-*isopropylamino*-3-*isopropyliminocyclohexene* (3·5 g.), b. p. 146—148°/19 mm., n_D^{15} 1·464 (Found: C, 45·4; H, 4·5; N, 8·3; F, 41·3. $C_{12}H_{15}F_7N_2$ requires C, 45·0; H, 4·7; N, 8·7; F, 41·6%).

Undecafluorocyclohexane (51·0 g.) and isopropylamine (100 c.c.) were kept in ether (150 c.c.) for 16 hr. to give the same amino-imine (43·4 g.), b. p. 103—104°/10 mm., n_D^{15} 1·463.

Oxidation of the Heptafluoro-1-*isopropylamino*-3-*isopropyliminocyclohexene*.—The normal procedure afforded di-(*S*-benzylthiouronium) hexafluoroglutarate (49%), m. p. 189° (Found: C, 44·4; H, 3·9%).

Hydrolysis of 2,4,4,5,5,6,6-*Heptafluoro*-1-*isopropylamino*-3-*isopropyliminocyclohexene*.—This compound (16·4 g.) and 2N-hydrochloric acid (500 c.c.) were kept at 10—15° for 16 hr. The precipitate was crystallised from aqueous ethanol to give 2,4,4,5,5,6,6-*heptafluoro*-1-*isopropylaminocyclohexen*-3-*one* (12·0 g.), m. p. 92° (Found: C, 38·4; H, 2·7; F, 47·7; N, 4·9. $C_9H_8F_7NO$ requires C, 38·7; H, 2·9; F, 47·7; N, 5·0%).

The amino-ketone was oxidised in the usual way to give hexafluoroglutaric acid which was characterised as its di-(*S*-benzylthiouronium) salt (52%), m. p. 189° (Found: C, 44·2; H, 3·7; N, 9·9%), and its dianilinium salt, m. p. 218° (Found: C, 47·9; H, 3·8%).

Tetrafluoro-m-*phenylenediamine*.—1-Aminoheptafluoro-3-iminocyclohexene (15·0 g.), ethanol (250 c.c.), Raney nickel (grade W4; 18 g.), and amberlite resin (IRA 400 standard grade; 10 g.) were shaken together in an atmosphere of hydrogen until *ca.* 3½ l. of hydrogen had been consumed. The mixture was then filtered and evaporated to leave a brown solid (6·2 g.) which was crystallised from water to give *tetrafluoro*-m-*phenylenediamine* (3·0 g.), m. p. 126—127° alone and in admixture with a specimen prepared by the reaction of pentafluoroaniline with ammonia[5] (Found: C, 40·3; H, 2·2; F, 41·8. $C_6H_4F_4N_2$ requires C, 40·0; H, 2·2; F, 42·2%); $\nu_{max.}$ 3460, 3350, 1675, and 1641 (NH_2), 1615 and 1520 cm.$^{-1}$ (benzene ring). The n.m.r. spectrum [Mullard SL mark 2 instrument, 30·107 mc./sec.] of a 3M-solution in acetone consisted of three peaks of intensity ratio 1:1:2. The diamine (0·2 g.), anhydrous ether (2 c.c.), and trifluoroacetic anhydride (1 c.c.) gave the *bis*(*trifluoroacetyl*) *derivative* (0·3 g.), m. p. 170—172° (from benzene) (Found: C, 32·3; H, 0·4; F, 50·8. $C_{10}H_2F_{10}N_2O_2$ requires C, 32·3; H, 0·5; F, 51·1%).

Perfluoro-m-*xylene*.—Perfluoro-1,3-dimethylcyclohexane (18·0 g.) was defluorinated in the usual way[7] at 460° to give unchanged starting material (9·7 g.) and perfluoro-*m*-xylene (3·4 g.), b. p. 119—120°, n_D^{17} 1·3621 (Found: C, 33·5. C_8F_{10} requires C, 33·6%); $\nu_{max.}$ 1682, 1657, and 1536 cm.$^{-1}$ (aromatic ring).

Tetrafluoroisophthalic acid.—Perfluoro-*m*-xylene (6·4 g.) was treated with fuming sulphuric acid (6·5 c.c.) as for its isomers.[7] Sublimation (150°/0·1 mm.) of the solid (2·7 g.) obtained gave *tetrafluoroisophthalic acid*, m. p. 203° (decomp.) (Found: C, 40·2; H, 0·8; F, 31·2. $C_8H_2F_4O_4$ requires C, 40·3; H, 0·8; F, 31·9%). The acid (0·2 g.) gave a *di*-(S-*benzylthiouronium*) *salt* (0·15 g.), m. p. 196° (decomp.) (from water) (Found: C, 50·3; H, 3·9; F, 13·6. $C_{24}H_{22}F_4N_4O_4S_2$ requires C, 50·5; H, 3·9; F, 13·3%).

The acid (6·05 g.) and phosphorus pentachloride (11·6 g.) were kept at 110° for 2½ hr.; phosphorus oxychloride was then removed by distillation and ether added to the residue. The ether solution was filtered and evaporated to leave tetrafluoroisophthaloyl chloride (4·0 g.) as a high-boiling liquid which was not further purified. A portion (0·22 g.) was shaken with phenol (0·16 g.), sodium hydroxide (0·15 g.), and water (5 c.c.) to give *diphenyl tetrafluoroisophthalate* (0·14 g.), m. p. 109° (from alcohol) (Found: C, 61·4; H, 3·0. $C_{20}H_{10}F_4O_4$ requires C, 61·5; H, 2·6%).

The acid chloride (3·8 g.) in acetone (25 c.c.) was shaken with sodium azide (0·98 g.) in water

(5 c.c.) at 0° for 15 min. When the blue-coloured lower layer was separated it decomposed violently to leave a brown intractable solid (0·5 g.), m. p. 290°, containing fluorine and nitrogen.

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