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FLUOROCYCLOPENTANES—V[1]*

LITHIUM ALUMINIUM HYDRIDE REDUCTION OF OCTAFLUORO-, 1,2-DICHLOROHEXAFLUORO-, AND 1-CHLOROHEPTAFLUORO-CYCLOPENTENE AND 1H,2-CHLORO-OCTAFLUOROCYCLOHEXENE

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Abstract—Octafluorocyclopentene, with LAH in diethyl ether, gave 1H- and 3H-heptafluorocyclopentene, 1H,2H-, 1H,3H- and 1H,5H-hexafluorocyclopentene, 1H,2H,3H- and 1H,5H,5H-pentafluorocyclopentene, and 1H,2H,3H,3H- and 1H,4H,5H,5H-tetrafluorocyclopentene. 1,2-Dichlorohexafluorocyclopentene, with LAH in diethyl ether gave 1H,2-chlorohexafluoro- and 1-chloro-5H,5H-pentafluoro-cyclopentene as the major products. With the same reagent, 1-chloroheptafluorocyclopentene gave 1H,2-chlorohexafluorocyclopentene as the major product. Similar reduction of 1H,2-chloro-octafluorocyclohexene gave 1H,2H-octafluorocyclohexene, and 1-chloro-6H,6H- and 1H, 6H,6H-heptafluorocyclohexene

Reductions of polyfluorocyclohexenes[2–5] and perfluorocyclobutene[6] with LAH in diethyl ether, and of polyhalogenated cyclo-butenes and -pentenes[7] with sodium borohydride in diglyme, have been described. We now report the LAH reduction of octafluoro-, 1-chloroheptafluoro-, and 1,2-dichlorohexafluorocyclopentene, and 1H,2-chloro-octafluorocyclohexene. As in the reductions described previously, the products can be derived by a reaction pathway consisting of a repetition of the sequence involving nucleophilic attack, resulting effectively in the transfer of hydride ion to olefinic carbon (C-1) and loss of halide ion from C-1 or from the allylic position C-3. The new olefin then being further attacked by the hydride until all the reagent is used up or the new olefin is unreactive. Octafluorocyclopentene (I) with LAH in diethyl ether gave five products (III, IV, VI, VII, VIII) which were separated by gas chromatography and characterized by oxidation and spectroscopy. The first component to emerge from the chromatography tube (III), shown by elemental analysis and mass spectrometry to be $C_5H_2F_6$, was oxidized by potassium permanganate to hexafluoroglutaric acid showing it to be 1H,2H-hexafluorocyclopentene. Support for this

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[1] Part IV. A. Bergomi, J. Burdon, T. M. Hodgins, R. Stephens, and J. C. Tatlow, *Tetrahedron* under consideration.

[2] J. A. Godsell, M. Stacey, and J. C. Tatlow, *Tetrahedron* **2**, 193 (1958).

[3] E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.* 3800 (1960).

[4] D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.* 4828 (1963).

[5] W. J. Feast and R. Stephens, *J. Chem. Soc.* 3502 (1965).

[6] G. Fuller and J. C. Tatlow, *J. Chem. Soc.* 3198 (1961).

[7] D. J. Burton, and R. L. Johnson, *J. Amer. Chem. Soc.* **86**, 5361 (1964); and *Abstracts* 148th. *Meeting Amer. Chem. Soc.* p12K (1964).

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structural allocation was provided by IR and proton- and 19F-NMR spectroscopy.[8] The second component (IV), present in trace amounts only, was shown by IR spectroscopy to be the known 1H,5H-hexafluorocyclopentene.[10] The third component (VI), $C_5H_3F_5$, was oxidized by acid permanganate at room temperature to 2H,2H-tetrafluoroglutaric acid. The IR, ^{1}H- and ^{19}F-NMR, and mass[9] spectra of component (VI), together with its formation from 1H,2H-hexafluorocyclopentene with LAH confirm that it is 1H,5H,5H-pentafluorocyclopentene. The fourth component (VII), $C_5H_3F_5$, was converted by acid permanganate to 1H-pentafluoroglutaric acid[11,12] showing it to be 1H,2H,3H-pentafluorocyclopentene. Support for this structure was provided by IR, and ^{19}F-NMR spectroscopy and mass spectrometry together with the formation of VII from 1H,5H- or 1H,3H-hexafluorocyclopentene, IV and IX respectively, with LAH. The fifth component (VIII), $C_5H_4F_4$, was oxidized by acid permanganate at

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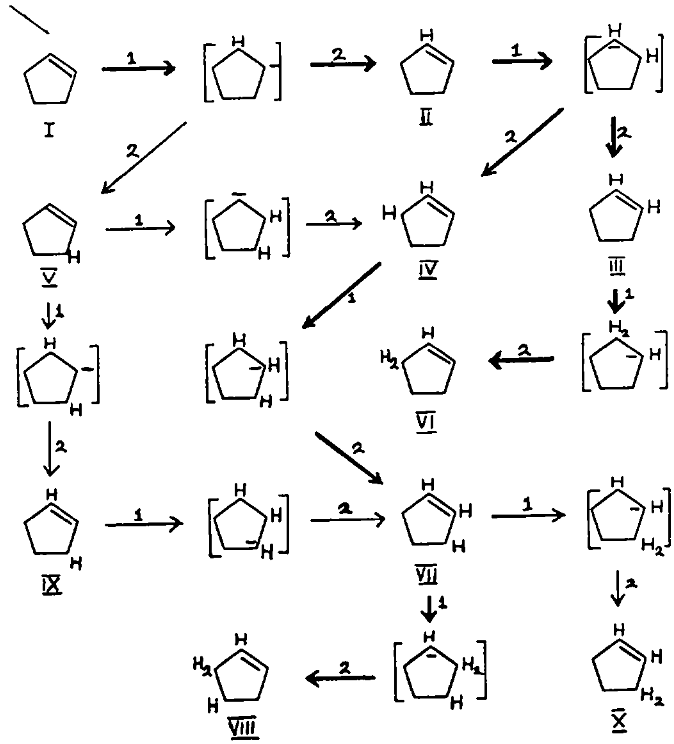

All unmarked substituents are fluorine

Reagents: 1,LAH; 2, loss of F⁻.
(Pathway of C_5F_8–LAH reaction traced by thick arrows.)

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[8] L. F. Thomas, unpublished work.

[9] J. R. Majer, unpublished work.

[10] J. Burdon, T. M. Hodgins, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 2382 (1965).

[11] A. K. Barbour, H. D. Mackenzie, M. Stacey and J. C. Tatlow, *J. Appl. Chem.* **4**, 341 (1954).

[12] R. J. Heitzman, C. R. Patrick, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 281 (1963).

room temperature to 2,2,3-trifluoroglutaric acid. The IR and ^{19}FNMR spectra of component VIII, together with its formation as major product from 1H,2H,3H-pentafluorocyclopentene (VII) with LAH confirms that it is 1H,4H,5H,5H-tetrafluorocyclopentene.

No mono-hydropolyfluorocyclopentenes were isolated from the reduction of octafluorocyclopentene with LAH in diethyl ether, because of the near coincidence of the gas chromatographic retention times of these olefins and this ether. However, when the reduction was carried out in tetrahydrofuran the known[12] 1H- and 3H-heptafluorocyclopentenes II and V, respectively, were isolated, the latter (V) in trace amounts.

When 3H-heptafluorocyclopentene (V) was treated with LAH in diethyl ether, the products separated by gas chromatography were: the known[10] 1H,3H- and 1H,5H-hexafluorocyclopentene IX and IV, respectively, component X, $C_5H_4F_4$, 1H,2H,3H-pentafluorocyclopentene (VII), and 1H,4H,5H,5H-tetrafluorocyclopentene (VIII). Component X was also formed, together with VIII, when VII was treated with LAH in diethyl ether. Hence, X must be 1H,2H,3H,3H-tetrafluorocyclopentene and this was confirmed by IR spectroscopy and mass spectrometry.[9] The olefins IX and X, however, were not isolated from the reaction of octafluorocyclopentene with LAH, presumably being present only in trace amounts.

1,2-Dichlorohexafluorocyclopentene with LAH in diethyl ether at 0° gave a complex mixture consisting of one major and at least six minor products. However, owing to the closely similar gas chromatographic retention times of the latter components, only the major product was obtained pure. When the reduction was carried out with an excess of 1,2-dichlorohexafluorocyclopentene at $-55°$, the known[7] 1H,2-chlorohexafluorocyclopentene was obtained, its structure was independently confirmed by its oxidation to hexafluoroglutaric acid, and by IR and ^{19}F NMR spectroscopy and mass spectrometry.[9]

The major product from the reduction at 0° was shown to be 1-chloro-5H,5H-pentafluorocyclopentene since on oxidation, with potassium permanganate in acetone, it gave tetrafluorosuccinic acid, and with acid permanganate at room temperature, it gave 2H,2H-tetrafluoroglutaric acid. Support for this structure was provided by IR and ^{19}F NMR spectroscopy and mass spectrometry.[9] This dihydro-olefin must arise from 1H,2-chlorohexafluorocyclopentene by the initial attack of the reagent at C-1; i.e., at the position of highest electron density in the ground state of the molecule. However, the result may be rationalized on the basis of intermediate carbanion stabilities; one bearing an α-chlorine substituent being favoured over one bearing an α-hydrogen.[13]

1-Chloroheptafluorocyclopentene with LAH in diethyl ether gave essentially 1H,2-chlorohexafluorocyclopentene and trace amounts of an unidentified component. This result can likewise be rationalized in terms of intermediate carbanion stability, the one bearing an α-chlorine being prefered to the one bearing an α-fluorine. Since the reduction of 1H-heptafluorocyclopentene and 1H-nonafluorocyclohexene[5] involve exclusive attack at C-2 it would appear that, provided the inductive effects of the groups in positions allylic to the double bond are similar in magnitude and direction, reduction of unsymmetrical polyhalo-olefins proceeds predominantly through the

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[13] J. D. Park, J. R. Dick and J. H. Adams, *J. Org. Chem.* 30, 400 (1965).

most stable carbanion; the order of stability being: $>\overset{\ominus}{C}—Cl > >\overset{\ominus}{C}—H > >\overset{\ominus}{C}—F$ The need for the conditional clause in this generalization was clearly emphasized, for example, by the reduction of 1-chloro-5H,5H-pentafluorocyclopentene with LAH in diethyl ether. This reaction gave only one product which was identified by IR spectroscopy as 1H,5H,5H-pentafluorocyclopentene; here the considerable differences in inductive power between the two allylic groups (—CF_2— and —CH_2—) make the ground state electron density the decisive factor in directing the entering nucleophile.

Similar observations were made with the analogous cyclohexene systems. Thus, 1H,2-chloro-octafluorocyclohexene with LAH in diethyl ether gave 1H,2H-octafluorocyclohexene,[5] 1-chloro-6H,6H- and 1H,6H,6H-heptafluorocyclohexene[5] in the ratio of 1:460:140, respectively. The structure given for the major component was indicated by its mode of formation and its oxidation, with acid permanganate at room temperature, to 2H,2H-hexafluoroadipic acid and confirmed by IR and ^{19}F NMR spectroscopy[8] and mass spectrometry.[9] As expected, 1-chloro-6H,6H-heptafluorocyclohexene with LAH in diethyl ether gave only 1H,6H,6H-heptafluorocyclohexene.

EXPERIMENTAL

Techniques. Oxidations, gas chromatography, and spectroscopic measurements were carried out as before,[1] unless otherwise stated. Known acids were characterized by two derivatives which had correct elemental analyses in each case reported.

The 19F NMR spectra were measured on a Mullard S.L. 44 Mk. 1 instrument at 30·107 mc/s and the figures quoted are fluorine chemical shifts and are in ppm from trifluoroacetic acid as external reference. The proton NMR spectra were measured on a Varian instrument at 60 mc/s and the figures quoted are chemical shifts in ppm from tetramethyl silane as external reference. Mass spectra were measured on a Metropolitan Vickers M.S.2 instrument.

Reaction of octafluorocyclopentene with lithium aluminium hydride

(a) *In diethyl ether.* Octafluorocyclopentene (I, 17·0 g) in diethyl ether (30 cc) was added dropwise during 35 min to a stirred suspension of LAH (4·2 g) in diethyl ether (30 cc) at 0°. When the initial reaction had subsided the mixture was stirred at 18° for 10 hr, then cooled to 0°, and water (10 cc) was cautiously added followed by 50% V/V HCl (30 cc) until no precipitate remained. After fractional evaporation (vacuum jacketed column, 1′ × ½″, packed with Dixon gauzes 1/16th″ × 1/16th) of the dried ($MgSO_4$) ethereal solution, the residue (23·1 g), b.p. > 34°, on gas chromatography (Column B, 80°, N_2 18 l/hr) gave: (i) diethyl ether (10·1 g); (ii) 1H,2H-*hexafluorocyclopentene* (III; 1·9 g), b.p. 77° (Found: C, 34·3; H, 1·3. $C_5H_2F_6$ requires: C, 34·1; H, 1·2%); (iii) (IV) (trace), with a correct IR spectrum;[10] (iv) 1H,5H,5H-*pentafluorocyclopentene* (VI; 5·7 g), b.p. 88°, (Found: C, 38·4; H, 1·8. $C_5H_3F_5$ requires: C, 38·0; H, 1·9%); (v) 1H,2H,3H-*pentafluorocyclopentene* (VII; 0·6 g), b.p. 100·5°. (Found: C, 38·1; H, 1·9%); (vi) 1H,4H,5H,5H-*tetrafluorocyclopentene* (VIII; 0·02 g), b.p. 103°, (Found: C, 42·7; H, 3·1. $C_5H_4F_4$ requires C, 42·9; H, 2·9%.)

(b) *In tetrahydrofuran.* LAH (0·9 g) in tetrahydrofuran (15 cc) was added during 40 min to a stirred solution of I (12·0 g) in tetrahydrofuran (10 cc) at 0°. A violet colouration developed and the mixture was stirred for 4 hr at 15°, then cooled to 0°, and water (10 cc) was cautiously added followed by 50% v/v HCl (20 cc) until no precipitate remained. The dried ($MgSO_4$) tetrahydrofuran layer was fractionally distilled (vacuum jacketed column, 1′ × ½″, packed with Dixon gauzes 1/16th″ × 1/16th″) The first fraction (4·8 g), b.r. < 60°, was separated by gas chromatography (Column B, 80°, N_2 15 l/hr) to give: (i) I (1·3 g); (ii) II (1·2 g), with a correct IR spectrum;[11] (iii) impure 3H-heptafluorocyclopentene (trace), identified by its IR spectrum.[11] Analytical gas chromatography of the distillation residue (10·1 g) indicated trace amounts of I and II together with 1H,2H-hexafluorocyclopentene and tetrahydrofuran.

1H,2H-*Hexafluorocyclopentene* (III). Compound II (10·0 g) and LAH (1·0 g) in diethyl ether were allowed to react in the manner described earlier to give: (i) II (0·6 g); (ii) diethyl ether (1·2 g); (iii) III (4·0 g); (iv) VI (2·1 g); and (v) VII (0·1 g).

Characterization of 1H,2H-*hexafluorocyclopentene* (III)

(a) *Oxidation.* The olefin (1·0 g), $KMnO_4$ (0·98 g) and acetone (98 cc) were shaken together for ¼ hr at 15° to give hexafluoroglutaric acid (66%).

(b) *Spectroscopy.* The olefin showed characteristically weak absorptions at 3110 cm^{-1} ($\geqslant$C—H) and 1640 cm^{-1} (—CH═CH—). The 19F NMR spectrum[8] showed two bands at 32·88 (relative intensity 2) and 55·31 (relative intensity 1). The proton NMR spectrum[8] at 100 Mc/s (Varian instrument) showed one band at 5·91. Mass spectrometry revealed a total mass peak of 176 ($C_5H_2F_6$) and the expected fragmentation pattern.[9]

1H,5H,5H-*Pentafluorocyclopentene* (VI). Compound III (5·0 g) and LAH (1·0 g) in diethyl ether, in the manner described earlier, gave: (i) ether (5·5 g); (ii) III (0·15 g); and (iii) VI (3·3 g).

Characterization of 1H,5H,5H-*pentafluorocyclopentene* (VI)

(a) *Oxidation.* Compound VI (3·1 g), $KMnO_4$ (3·4 g), water (200 cc) and conc H_2SO_4 (25 cc) were intimately mixed by means of a vibrator-type stirrer for 7 hr at 15°. Subsequent treatment was normal and gave a solid acid (2·1 g) which was sublimed to give 2H,2H-*tetrafluoroglutaric acid* m.p. 129–133°, (Found: C, 29·2; H, 2·1. $C_5H_4F_4O_4$ requires C, 29·4; H, 2·0%) which was characterized as its bis -*S-benzylthiouronium salt* m.p. 172–173°, (Found: C, 47·2; H, 4·5. $C_{21}H_{24}F_4N_4O_4S_2$ requires: C, 47·0; H, 4·5%.)

(b) *Spectroscopy.* Compound VI showed a strong absorption at 1693 cm^{-1} (—CH═CF—). The 19F NMR spectrum[8] showed bands at 37·69 (relative intensity 2) assigned to the F at C-4, 44·16 (relative intensity 2) assigned to the F at C-3, and at 62·70 (relative intensity 1) assigned to the F at C-2. The proton NMR spectrum[8] at 100 Mc/s showed bands at 2·83 (relative intensity 2) ascribed to the protons at C-5, and at 5·71 (relative intensity 1) ascribed to the proton at C-1. Mass spectrometry[9] revealed a total mass peak of 158 ($C_5H_3F_5$) and the expected fragmentation pattern.

1H,2H,3H-*Pentafluorocyclopentene* (VII). Compound IV (5·2 g) and LAH (1·45 g) in diethyl ether, in the manner described earlier, gave: (i) ether; (ii) 1H,2H,3H,3H-*tetrafluorocyclopentene* (X, 0·1 g); (iii) VII (2·0 g); (iv) VIII (0·75 g).

Characterization of 1H,2H,3H-*pentafluorocyclopentene* (VII)

(a) *Oxidation.* Compound VII (2·1 g), $KMnO_4$ (2·8 g), H_2SO_4 (22 cc) and water (170 cc) were intimately mixed by means of a vibrator-type stirrer for 7 hr at 15°. Subsequent treatment was normal and gave crude 2H-pentafluoroglutaric acid (1·8 g), characterized as its bis-S-benzylthiouronium salt.[11,12]

(b) *Spectroscopy.* Compound VII showed a weak absorption at 1635 cm^{-1} (—CH═CH—). The 19F NMR spectrum[8] consisted of two AB quadruplet systems centered at 32·05 (relative intensity 2) ($J = 8·77$) and 50·36 (relative intensity 2) ($J = 8·45$) assigned to the F at C-5 and C-4, respectively, and a doublet at 112·86 (relative intensity 1) ($J = 1·68$) assigned to the F at C-3. Mass spectrometry[9] revealed a total mass peak of 158 ($C_5H_3F_5$) and the expected fragmentation pattern.

1H,2H,3H,3H-*Tetrafluorocyclopentene* (X). Compound VII (2·0 g) and LAH (1·9 g) in diethyl ether, in the manner described previously, gave: (i) ether, (ii) X (0·16 g), (Found: C, 42·9; H, 2·8. $C_5H_4F_4$ requires: C, 42·9; H, 2·9%.) and (iii) VIII (0·45 g)

Characterization of 1H,2H,3H,3H-*tetrafluorocyclopentene* (X)

Spectroscopy. Compound X showed a weak absorption at 1630 cm^{-1} (—CH═CH—). Mass spectrometry[9] revealed a total mass peak of 140 ($C_5H_4F_4$) and the expected fragmentation pattern.

Characterization of 1H,4H,5H,5H-*tetrafluorocyclopentene* (VIII)

(a) *Oxidation.* Compound VIII (0·5 g), $KMnO_4$ (0·75 g), conc H_2SO_4 (6 cc) and water (125 cc) were intimately mixed by means of a vibrator-type stirrer for 9½ hr at 15°. Subsequent treatment was normal and gave a solid acid (0·2 g) which was sublimed to give 2,2,3-*trifluoroglutaric acid,* m.p. 91–101° which was characterized as its bis-S-*benzylthiouronium salt,* m.p. 164°, (Found: C, 48·8; H, 0·5. $C_{21}H_{23}F_3N_4O_4S_2$ requires: C, 48·6; H, 4·9%.)

(b) *Spectroscopy.* Compound VIII showed absorptions at 3000 cm^{-1} (⩾C—H) and 1700 cm^{-1}. (—CH═CF—). The 19F NMR spectrum[8] showed an AB quadruplet system centered at 35·82 (relative intensity 2) (J = 8·51) ascribed to the F at C-3, a band at 66·58 (relative intensity 1) ascribed to the F at C-2, and a doublet at 119·23 (relative intensity 1) (J = 3·31) ascribed to the F at C-4.

Reaction of 3H-*heptafluorocyclopentene* (V) *with lithium aluminium hydride*

Compound V (7·0 g) and LAH (2·4 g) in diethyl ether, gave: (i) diethyl ether; (ii) IX (trace);[10] (iii) IV (trace);[10] (iv) X (trace); (v) VII (2·3 g); (vi) VIII (0·5 g). All the products had correct IR spectra.

Reaction of 1,2-*dichlorohexafluorocyclopentene with Lithium aluminium hydride*

1,2-Dichlorohexafluorocyclopentene (33·8 g) in diethyl ether (80 cc) was added dropwise to a suspension of LAH (2·43 g) in diethyl ether (200 cc) at −55° (±5°) ("dri-Kold"/EtOH). After the usual isolation procedure, gas chromatography (column B, 100°, N_2 16 l./hr) gave: (i) diethyl ether (trace); (ii) 1,2-dichlorohexafluorocyclopentene (12·0 g) with a correct IR spectrum; (iii) 1H,2-chlorohexafluorocyclopentene (2·6 g), b.p. 80° (cited[7] 77·5°), (Found: C, 28·0; H, 0·7; Cl, 16·4. Calc. for $C_5HCl\,F_6$: C, 28·5; H, 0·5; Cl, 16·8%.)

(b) 1,2-Dichlorohexafluorocyclopentene (120 g) and LAH in diethyl ether (300 cc) at 0° gave, a product (84·8 g) which was separated by gas chromatography (Column A) to give: (i) a mixture of diethyl ether, 1,2-dichlorohexafluorocyclopentene, and 1H,2-chlorohexafluorocyclopentene (36·0 g); (ii) 1-*chloro*-5H,5H-*pentafluorocyclopentene* (37·4 g), b.p. 94°, (Found: C, 31·2; H, 1·2; Cl, 18·0. $C_5H_2Cl\,F_5$ requires: C, 31·2; H, 1·1; Cl, 18·4%); (iii) a complex mixture of minor products containing at least six components.

Characterization of 1H,2-*chlorohexafluorocyclopentene*

(a) *Oxidation.* The olefin (0·7 g), $KMnO_4$ (0·55 g) and acetone (70 cc) were shaken together for ½ hr and gave hexafluoroglutaric acid (82%).

(b) *Spectroscopy.* The olefin showed absorptions at 3090 cm^{-1} (> C—H) and 1640 cm^{-1} (—CH═C—Cl—, cited[7] 1635 and 1637 cm^{-1}). Mass spectrometry[9] revealed a total mass peak 210·46 ($C_5HCl\,F_6$) and the expected fragmentation pattern.

Characterization of 1-*chloro*-5H,5H-*pentafluorocyclopentene*

(a) *Oxidation.* (i) The olefin (1·07 g) and $KMnO_4$ (1·6 g) in acetone (200 cc) were shaken together for ½ hr and gave tetrafluorosuccinic acid (79%). (ii) The olefin (5·0 g), $KMnO_4$ (4·6 g), conc H_2SO_4 (40 cc) and water (520 cc) were intimately mixed by means of a "vibrator-type" stirrer for ½ hr at 18° and gave a glassy amber solid acid (5·15 g) which was sublimed (85°/1mm) to give 2H,2H-*tetrafluoroglutaric acid* m.p. 128°, (Found: C, 29·3; H, 2·4; Equiv., 102. $C_5H_4F_4O_4$ requires: C, 29·4; H, 2·0% Equiv., 102.)

(b) *Spectroscopy.* The olefin showed absorptions at 2965 cm^{-1} (⩾C—H) and 1710 cm^{-1} (—CF═CCl—). The 19F NMR spectrum showed three bands at 36·81 (relative intensity 2) assigned to the F at C-4, 41·35 (relative intensity 2) assigned to the F at C-3, and 65·01 (relative intensity 1) assigned to the F at C-2. Mass spectrometry[9] revealed a total mass peak of 192·46 ($C_5H_2Cl\,F_5$).

Reaction of 1-*chloro*-5H,5H-*pentafluorocyclopentene with lithium aluminium hydride*

1-Chloro-5H,5H-pentafluorocyclopentene (4·2 g) and LAH (0·82 g) in diethyl ether, gave a mixture shown by analytical gas chromatography and IR spectroscopy to be essentially 1-chloro-5H,5H-pentafluorocyclopentene together with 1H,5H,5H-pentafluorocyclopentene.

Reaction of 1-*chloroheptafluorocyclopentene with lithium aluminium hydride*

1-Chloroheptafluorocyclopentene (1·0 g) and LAH (0·3 g) in diethyl ether (50 cc) were stirred together for 1 hr at −78°. After the usual isolation procedure, analytical gas chromatography indicated two components. The major product was isolated by preparative gas chromatography [Column B] and was 1H,2-chlorohexafluorocyclopentene, with a correct IR spectrum; the trace component was not identified.

Reaction of 1H,2-*chloro-octafluorocyclohexene with lithium aluminium hydride*

1H,2-Chloro-octafluorocyclohexene[5] (14·8 g) and LAH (2·2 g) in diethyl ether, in the previously described manner, gave: (i) diethyl ether (trace); (ii) 1H,2H-octafluorocyclohexene (0·02 g), with a correct IR spectrum; (iii) 1-*chloro*-6H,6H-*heptafluorocyclohexene* (7·04 g), b.p. 116°, (Found: C, 29·4; H, 0·6 $C_6H_2Cl\,F_7$ requires: C, 29·7; H, 0·8%); (iv) 1H,6H,6H-heptafluorocyclohexene (0·55 g), with a correct IR spectrum.

Characterization of 1-*chloro*-6H,6H-*heptafluorocyclohexene*

Spectroscopy. The olefin showed absorptions at 2950 cm^{-1} ($\geqslant$C—H) and 1705 cm^{-1} (—CF=C—Cl—). The 19F NMR spectrum showed four bands at 40·82 (relative intensity 2), at 43·31 (relative intensity 2), at 56·00 (relative intensity 1) and at 59·75 (relative intensity 2). Mass spectrometry showed a top mass peak of 242·46 ($C_6H_2Cl\,F_7$) and the expected fragmentation pattern.

Reaction of 1-*chloro*-6H,6H-*heptafluorocyclohexene with lithium aluminium hydride*

1-Chloro-6H,6H-heptafluorocyclohexene (2·0 g), LAH (1·5 g) and diethyl ether (100 cc) were refluxed together for 24 hr. The usual isolation procedure gave a mixture, shown by analytical gas chromatography to contain one component in addition to diethyl ether. Preparative gas chromatographic separation of this mixture (col. B, 100°, N_2 16 l./hr) gave: (i) diethyl ether, and (ii) 1H,6H,6H-heptafluorocyclohexene (0·2 g) with a correct IR spectrum.

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