

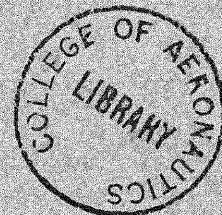
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THE COLLEGE OF AERONAUTICS  
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THE REACTION OF PERFLUOROGLUTARIC ACID WITH METHYL  
MAGNESIUM IODIDE PART II

by

D. A. Smith

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magnesium iodide Part II

- by -

D.A. Smith, M.Sc., F.R.I.C., A.P.I.

S U M M A R Y

Perfluoroglutaric acid when treated with methyl magnesium iodide afforded hexafluoro-2,6-dimethylpyran-2,6-diol in high yield and 2,2,3,3,4,4-hexafluoro-5-oxocaproic acid in low yield. The former appeared to exist in a range melting form (64-79°C) and also in a very labile form melting at 96-98°C. Problems associated with the formation of this latter form were investigated. The hexafluoro-2,6-dimethylpyran-2,6-diol yielded a monosemi-carbazone and also a mono and a di(2,4-dinitrophenylhydrazone). The mono (2,4-dinitrophenylhydrazone) appeared to be cyclic. Reduction, both with lithium aluminium hydride and sodium borohydride yielded 3,3,4,4,5,5-hexafluoro-n-heptane-2,6-diol. Reaction with anhydrous calcium sulphate gave 3,3,4,4,5,5-hexafluoro-2-methylcyclohex-1-ene-6-one.

The acid product of the original reaction of perfluoroglutaric acid and methyl magnesium iodide was characterised as a 2,4-dinitrophenylhydrazone and as an S-benzylthiouronium salt. Infra-red spectroscopic evidence suggests the latter compound exists in a straight chain form.

Contents

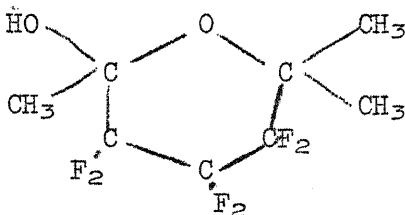
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The reaction of non-fluorinated carboxylic acids with Grignard compounds was reported by Huston and Bailey (1) and by Grignard (2). The major product was the corresponding tertiary alcohol, though low yields of ketone also occurred.

The reaction of the sodium salts of carboxylic acids with Grignard compounds was described by Salkind and Beburischwili (3). In this case ketones were obtained, but in yields below 25%.

The reactions of fluorinated carboxylic acids with Grignard compounds were described by Sykes, Tatlow and Thomas (4). The authors reported the reaction of anhydrous trifluoro acetic acid with a number of Grignard compounds R.Mg.X., where R was methyl, ethyl, isopropyl, n-butyl, tert-butyl, phenyl. The corresponding ketones (CF<sub>3</sub>.CO.R) were obtained in 40-60% yields. Optimum yields of ketone were obtained at a molar ratio of 2.5 moles of Grignard reagent to 1 mole of acid. There was no evidence for the formation of stable ketone hydrates and in all cases the haloform cleavage took a normal course. Dishart and Levine (5) also found that perfluoro monobasic carboxylic acids could be converted to ketones by the use of Grignard reagents. Groth (6) claimed that when methyl magnesium bromide reacted with perfluoroglutaric acid a cyclic hemi-ketal was formed.



In order to react perfluoroglutaric acid with methyl magnesium iodide and obtain reasonable yields it was necessary to dry the perfluoroglutaric acid by benzene azeotropic distillation and special methods were used to overcome iodine contamination. Both acid and neutral products were obtained, these were separated by fixing acids as sodium salts in the aqueous layer and removing neutral products by continuous ether liquid/liquid extraction. After removal of neutral products the aqueous layer was rendered acid, and the acid products similarly extracted using continuous ether liquid/liquid extraction. The neutral product, which melted over a range (64-79°C) was hexafluoro-2, 6-dimethylpyran-2, 6-diol(I) (HDPD) (See Fig. 1). Infra-red spectra supported this structure and N.M.R. evidence suggested a 4:1 mixture of cis and trans isomers. Gas chromatography (analytical) also suggested two forms of this compound.

The material distilled over a wide range, with considerable decomposition, and the compound was normally prepared by removal of ether, followed by recrystallisation.

The acid products gave a compound b.p.113-5°C which was 2,2,3,3,4,4 - hexafluoro-5-oxo-caproic acid (II) in a non-hydrated form. A pronounced carbonyl frequency was observed in the i.r. spectrum. The S-benzyl thiouronium salt had an i.r. spectrum with a marked likeness to that of the S-benzyl thio-uronium derivative of pentafluoropropionic acid. The evidence suggests the S-benzyl thiouronium salt is linear, and that the carbonyl group is non-hydrated. A similar case is recorded by Sayers, Stephens and Tatlow (7), who found that the S-benzyl salt of 2,2,3,3,4,4,5,5-octafluoro-6-oxo-heptanoic acid showed a carbonyl frequency in the infra-red i.e. the carbonyl group was non-hydrated.

Hexafluoro-2,6-dimethylpyran-2,6-diol formed a mono semi-carbazone III m.p.201-2°C which was linear, the carbonyl group being hydrated (i.r. analysis showed strong hydroxyl and no carbonyl frequency). Hexafluoro-2,6-dimethylpyran-2,6-diol formed a mono-2,4-clinitrophenyl hydrazone (IV) (m.p.140-1°) and a di-2,4-dinitrophenyl hydrazone (V)(m.p.203-4°). Infra-red evidence suggested that the mono-compound was cyclic, but the di-compound was linear. It is not entirely clear why the carbonyl group of the mono-semicarbazone is hydrated, whereas the mono-2,4-dinitrophenyl hydrazone is cyclic. This may be connected with the fact that the -NH group in 2,4-DNPH's is amine-like whereas in semi-carbazone it is amide-like.

Hexafluoro-2,6-dimethylpyran-2,6-diol merely charred when reacted with most standard dehydrating agents. When distilled off calcium sulphate 3,3,4,4,5,5-hexafluoro-2-methylcyclohex-1-ene-6-one(VI) was obtained. This material is formed with water, so the function of the calcium sulphate may be catalytic. N.M.R., ultra-violet and infra-red evidence was consistent with the proposed structure.

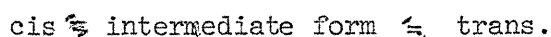
Reduction of hexafluoro-2,6-dimethylpyran-2,6-diol using lithium aluminium hydride and also sodium borohydride gave the same product in both cases, 3,3,4,4,5,5-hexafluoro-n-heptane-2,6-diol (VII)(m.p.54-68°). The compound may be supposed to have D,L, meso and racemic forms, which would explain the melting range, but this point was not investigated.

The acid product 2,2,3,3,4,4-hexafluoro-5-oxo-caproic acid gave a 2,4-dinitrophenyl hydrazone (VIII)(m.p. 124°C) and also an S-benzyl thiouronium salt (IX)(m.p.144-5°C). Infra-red analysis of the S-benzyl thiouronium salt showed a carbonyl frequency, suggesting the carbonyl group is not hydrated in this compound.

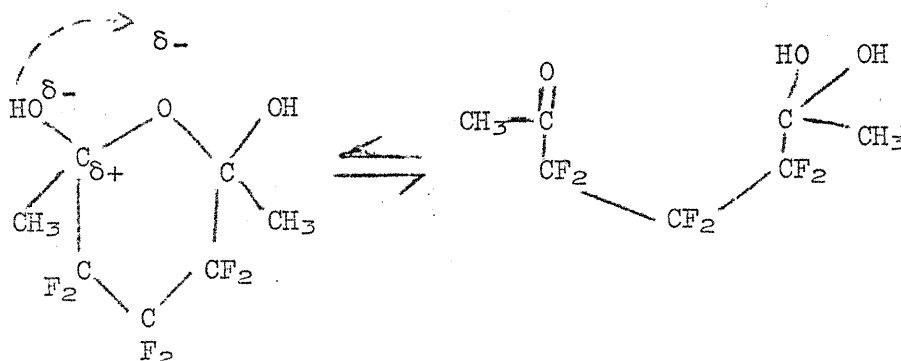
As stated, Hexafluoro-2,6-dimethyl pyran-2,6-diol (HDPD), as prepared by either recrystallisation or distillation has a melting range 64-79°C. This is explained by the existence of cis and trans forms. Rigby (8) separated cis and trans forms of cyclohexane-1,3-diol using fractional recrystallisation from acetone, and attempts were made to separate the cis and trans forms of HDPD by recrystallisation processes from toluene, benzene, petroleum and chloroform. Under some circumstances, which were not readily reproducible, a material of m.p.96-98°C crystallised out, once this had started to form successive crops could be obtained by evaporation of mother

liquors. If it did not form initially it did not appear after further evaporation and recrystallisation. Apart from materials melting at 64-79°C, materials of intermediate forms melting in the 80's were also noted. Investigation showed that these phenomena were not directly linked either with the presence of water in the solvents, or with the relative humidity of the atmosphere in which the recrystallisation experiments were performed. The 96-98° melting form was stable in moist air for several days, at room temperature, but within 2-3 weeks returned to the 64-79°C melting range form. This process was accelerated by increased temperature (45°C). Mechanical means, such as prolonged shaking or pressing through a fine sieve brought about an accelerated conversion of the 96-98°C melting form to the 64-79°C melting range form. Attempts were also made to 'lock' the *cis* form as an internal malanoate or carbonate, but these were not successful.

A tentative explanation of these phenomena is offered on the following lines. If the 96-98°C melting form were the *cis* compound, say, one would expect during recrystallisation that the mother liquors would become increasingly rich in the *trans* form, which would be expected to have a different melting point. In fact this does not occur. It may be postulated that the *cis* and *trans* forms give a continuous series of solid solutions, having a curve such, that the solidus and liquidus curves meet at a point. (See fig. 2). At this point there is a sharp melting point, similar to a simple compound. If a mixture of *cis* and *trans* material occurred in the correct proportions a material of sharp melting point would crystallise, otherwise various range melting materials would appear. In addition it is necessary to postulate that there is an equilibrium between *cis* and *trans* forms in the solid phase, i.e. that there is solid phase tautomerism.



It may be supposed that under given conditions there is a certain ratio of *cis* to *trans* forms, depending on the equilibrium constant. This explains why the stable form of HDPD is eventually always a form melting at a particular range (64-79°C). Other range forms, and the 96-98°C melting form are unstable, because they are based on non equilibrium proportions of *cis* and *trans* materials. For reasons not understood, the transition to the equilibrium form is favoured by the absorption of mechanical, as well as thermal energy. Neither is it understood how the correct proportions for a 96-98°C melting point form are arrived at. For the *cis* form to change into the *trans* a carbon-oxygen band in the pyranose ring must be broken and reformed.



The straight chain form intermediate would then change back into the ring form, but the cis form of the ring compound would be favoured due to internal hydrogen bonding. The presence of electronegative fluorine atoms may favour the bond polarisations leading to ring breakage, certainly ketone type derivatives are formed with little difficulty. The interchange between cis and trans forms could also occur in the solid state making separation of the forms extremely difficult due to interconversion. There is some analogy to the chemistry of glucose and solid phase tautomerism has been postulated in certain acridine compounds. 9,10,11.

#### Experimental section

Melting points were performed on a Gallenkamp Melting Point Apparatus, and are uncorrected. I.r. spectra were performed on a Perkin-Elmer Infracord 137 instrument and were normally done as Nujol mulls.

#### Reaction of Perfluoroglutaric Acid with Methyl Magnesium iodide

Molar ratio; 8 moles methyl magnesium iodide to 1 mole perfluoroglutaric acid.

Perfluoroglutaric acid (24g.) was dissolved in benzene (200 ml.) and dried azeotropically using a Dean and Stark trap. Benzene was removed by distillation and the perfluoroglutaric acid dissolved in ether (200 ml. sodium dried). The solution was dried ( $\text{Na}_2\text{SO}_4$ ). Methyl iodide was redistilled and dried ( $\text{Na}_2\text{SO}_4$ ). Magnesium (19.4g dried  $100^\circ\text{C}$ , 3 hr), was treated with methyl iodide (114g.) dissolved in ether (200g. sodium dried) and after the reaction had subsided the materials were refluxed for  $1\frac{1}{2}$  hours. Perfluoroglutaric acid (dried, 24g. dissolved in 200 ml. sodium-dried ether) was added to produce a fluid slurry. The slurry was refluxed for  $2\frac{1}{4}$  hours. Distilled water (40 ml.) was added, with cooling, followed by hydrochloric acid (140 ml. 50% aq. solution). Sodium bicarbonate (solid) was added until the aq. layer was alkaline to litmus. Sodium thiosulphate (solid) was added and the ethereal and aqueous layers shaken for  $\frac{3}{4}$  hour, or until the brown colour of the ether layer was discharged.

The ether layer was separated, and using the ether layer the aqueous part was continuously extracted for 16 hours. The resultant ethereal solution was dried ( $\text{Na}_2\text{SO}_4$ ), decolourised (charcoal) and de-iodised (ppt. silver). Ether was removed by distillation and evaporation and the crude natural product purified by recrystallisation from benzene or petroleum. The alkaline aqueous layer was acidified (sulphuric acid) and continuously extracted with ether for 16 hours. The ethereal extract was dried ( $\text{Na}_2\text{SO}_4$ ), decolourised (charcoal) and de-iodised (ppt. silver). Ether was distilled off and the acid product obtained by vacuum distillation.

#### Neutral product Hexafluoro-2,6-dimethylpyran-2,6-diol (HDPD)

The neutral product (18.2g.) and m. range  $64-79^\circ$ , also distilled at approximately  $80^\circ\text{C}$  at 19 mm and at  $70-115^\circ\text{C}$  at atmospheric pressure. In the

i.r. spectrum no carbonyl frequency but pronounced hydroxyl frequencies were observed. Proton n.m.r. spectrum of an ether solution showed two groups of peaks, one broad at 6.2 p.p.m. and another at 1.5 p.p.m. ( $\text{CH}_3$ ) in approximately 1:3 ratio. In the  $\text{CH}_3$  region there were two groups of peaks in ratio 4:1 each of which was further split. This indicates a 4:1 mixture of cis and trans isomers and the data cannot be interpreted in terms of a single structure.

Using a Perkin-Elmer 452 g.l.c. apparatus and a silicone gum column ( $150^\circ$ ) an ethereal solution gave, apart from the ether peak, a second peak that was partially resolved into two peaks.

Distilled material solidified to give a solid m. range  $64-79^\circ$  (Found C, 32.8; H, 3.1.  $\text{C}_7\text{H}_8\text{F}_6\text{O}_3$  requires C, 33.1; H, 3.2%).

Recrystallised from 80-100 petroleum gave also a solid m. range  $64-79^\circ$  (Found C, 3.27%; H, 3.1,  $\text{C}_7\text{H}_8\text{F}_6\text{O}_3$  requires C, 33.1; H, 3.2%). Yields of product; 8 moles methyl magnesium iodide to 1 mole perfluoroglutaric acid 70.5%, 16 moles methyl magnesium iodide to 1 mole acid, 74.8%, and at 4 moles methyl magnesium iodide to 1 mole acid, 30.1%.

Acid Product 2,2,3,3,4,4 - hexafluoro-5-oxo-caproic acid

The acidic product (1.2g) was distilled (b.p.  $112^\circ$  at 13.5 mm.). Found C, 29.3; H, 2.1.  $\text{C}_6\text{H}_4\text{F}_6\text{O}_3$  requires C, 30.3; H, 1.7%). The i.r. spectrum showed a strong carbonyl absorption band  $1760\text{ cm}^{-1}$ .

HDPD di-(2,4-dinitrophenylhydrazone)

HDPD in acid methanol, treated with 2,4-dinitro phenylhydrazine afforded a di-(2,4-dinitrophenylhydrazone) (m.p.  $203-4^\circ$ , bright yellow). Found C, 38.1; H, 2.6.  $\text{C}_9\text{H}_4\text{F}_6\text{N}_8\text{O}_8$  requires C, 38.3; H, 2.4%). I.r. spectrum showed  $\text{-C=N-}$  stretching frequency at  $1630\text{ cm}^{-1}$ .

HDPD mono-(2,4-dinitrophenylhydrazone)

HDPD (1 mole) in acidic methanol, treated with 2,4-dinitrophenylhydrazine afforded a mono-(2,4-dinitrophenylhydrazone) (m.p.  $140-1^\circ$ , brown). Found C, 37.7; H, 2.4.  $\text{C}_{13}\text{H}_{10}\text{F}_6\text{N}_4\text{O}_5$  requires C, 37.5; H, 2.4%). I.r. spectrum showed  $\text{-C=N-}$  stretching frequency at  $1630\text{ cm}^{-1}$  but no carbonyl frequency.

HDPD mono-semicarbazone

Semi-carbazide hydrochloride (0.2g) was dissolved in sodium acetate solution (10 ml. saturated) and HDPD (0.1g m. range  $64-79^\circ$ ) was dissolved in this solution and refluxed for  $\frac{1}{2}$  hour. Cooled ( $-12^\circ\text{C}$ , 2 days), crystals washed (water) and dried (in vacuo,  $\text{P}_2\text{O}_5$ , 16 hours), to give compound m.p.  $201-2^\circ$ . I.r. spectrum showed a broad  $\text{-C=N-}$  band at  $1700\text{ cm}^{-1}$  similar to that in 1,1,1-trifluoro acetone semi-carbazone. There was no carbonyl frequency.



3,3,4,4,5,5-hexafluoro-n-heptane-2,6-diol (1st method)

Lithium aluminium hydride (1.5g) was made into a slurry using ether (sodium dried). HDPD (3g. m. range 64-79°) was dissolved in ether (30 ml. sodium dried) and this was mixed with the lithium aluminium hydride slurry, stirred (r.t. 24 hours) and refluxed (24 hours). Water (12 ml. distilled) was added to the ether layer, then sulphuric acid (50 ml. 20% aqueous solution). The ether layer was separated, washed (20 ml. 20% sulphuric acid, 20 ml. distilled water), dried (Na<sub>2</sub>SO<sub>4</sub>, 16 hr.) and decolourised (charcoal). Ether was distilled off under reduced pressure, leaving an oil which solidified at -12°C to afford a material of m. range 56-65°C. Recrystallised from 80-100 petroleum (0.3g. m. range 56-61°C). I.r. spectrum contained strong hydroxyl and no carbonyl absorption. Found C, 35.0; H, 4.1. C<sub>7</sub>H<sub>10</sub>F<sub>6</sub>O<sub>2</sub> requires C, 35.0; H, 4.2%.

3,3,4,4,5,5-hexafluoro-n-heptane-2,6-diol (2nd method)

HDPD (3g. m. range 64-79°) was dissolved in water (90 ml.). Undissolved material was separated off and sodium borohydride (1.5g) was dissolved in the solution, and left for 5 days. The solution was acidified (dil. sulphuric acid) and extracted with ether continuously for 24 hr. The ether extract was dried (Na<sub>2</sub>SO<sub>4</sub>), ether distilled off and the residue recrystallised from 80-100 petroleum (decolourised with charcoal), to give a material m. range 52-64° (0.7g). The material was recrystallised from 80-100 petroleum (0.3g. m. range 54-68°, mixed m.p. with material from Method 1, 55-66°). I.r. spectrum was identical with material prepared using lithium aluminium hydride. Found C, 35.0; H, 4.3; C<sub>7</sub>H<sub>10</sub>F<sub>6</sub>O<sub>2</sub> requires C, 35.0; H, 4.2%.

3,3,4,4,5,5-hexafluoro-2-methylcyclohex-1-ene-6-one

HDPD was mixed with calcium sulphate (30 g. dried 16 hr. at 650°C) in dried apparatus and refluxed for 15 minutes. Liquid distilling at 94-96° was collected and separated into two layers, which did not mix after 2 days. Layers were separated, upper layer n<sub>D</sub><sup>21</sup> 1.3751, lower layer n<sub>D</sub><sup>21</sup> 1.3343. The lower layer proved to be water. (n<sub>D</sub><sup>21</sup> of molten HDPD 1.3523), upper layer yield .03g., found C, 40.1; H, 1.9 C<sub>7</sub>H<sub>4</sub>F<sub>6</sub>O requires C, 38.6; H, 1.9%. I.R. spectrum showed carbonyl absorption at 1700 cm<sup>-1</sup> and -C=C- at 1600 cm<sup>-1</sup>. N.m.r. spectrum showed two peaks, one at 2.2 p.p.m. (CH<sub>3</sub>) and the other at 6.4 p.p.m. (H adjacent to double bond) in ratio 3:1. This is consistent with the proposed structure. U.v. spectrum had bands 238 mμ, log ε 3.88, and at 279 mμ, log ε 3.31. Quoted for 3-methylcyclohex-2-ene-1-one a peak at 232 mμ, log ε 4.04. Comparison with the hydrocarbon analogue supports the proposed structure.

Haloform reaction

Products of the haloform reaction could not be characterised with certainty, but fluoride ion was detected after 2 hr. reflux of HDPD with N caustic soda. (Cerous nitrate method).

2,2,3,3,4,4-hexafluoro-5-oxo-caproic acid 2,4-dinitrophenylhydrazone

2,2,3,3,4,4-hexafluoro-5-oxo-caproic acid was reacted with an excess aqueous acidic solution of 2,4-dinitrophenylhydrazone to give yellow crystals m.p. 124°. Sodium fusion test indicated the presence of nitrogen and fluorine. Found C, 34.2, H, 2.3. C<sub>12</sub>H<sub>8</sub>F<sub>6</sub>N<sub>4</sub>O<sub>6</sub> requires C, 34.5; H 1.9%.

2,2,3,3,4,4-hexafluoro-5-oxo-caproic acid, S benzylthiuronium salt

The S benzyl thio-uronium salt was prepared in the usual way and recrystallised (80% ethanol) and dried (vacuo, P<sub>2</sub>O<sub>5</sub>, 16 hr.) to give a compound m.p. 144-5°. I.r. analysis showed a carbonyl peak at 1760 cm<sup>-1</sup> similar to that in S-benzylthiuronium pentafluoropropionate. Found C, 30.9; H, 3.3. C<sub>14</sub>H<sub>14</sub>F<sub>6</sub>N<sub>2</sub>O<sub>3</sub>S requires C, 31.3; H, 3.5%.

Different Crystalline forms of Hexafluoro-2,6-dimethylpyran-2,6-diol (HDPD)

Systematic recrystallisation of this material (m. range 64-79°) were undertaken from chloroform, benzene, toluene and 80-100 petroleum. From chloroform were obtained forms of melting ranges 92-94°, 97-98°, 98-99°, 83-85°, 91-94°. From benzene forms of melting ranges 95-97°, 94-95°, 95-96°, 90-93° and 88-90° were obtained. From toluene forms of melting ranges 92-94°, 94-95°, 96-99°, 96-97°, 97-98° and 93-95° were obtained. From 80-100 petroleum forms of melting ranges 78-79°, 80-81°, 84-86°, 90-91°, 86-89° were obtained. Numerous repetitions of these experiments sometimes only yielded the standard form of melting range 64-79°. If a high melting form appeared in the first crop it could be formed in subsequent crops, if it did not appear initially it did not appear at all.

HDPD recrystallised from 80-100 petroleum, having an original m. range of 64-79°, had a m. range of 96-98° after recrystallisation and a m. range of 64-79° after subsequent ageing. Found C 32.7; H, 3.1, C<sub>7</sub>H<sub>8</sub>F<sub>6</sub>O<sub>3</sub> requires C, 33.1; H, 3.2%.

HDPD was recrystallised from 1-dichloro-monofluoro-2-monochloro-2-difluoroethane (initial m. range 64-79°, after recrystallisation 95-96°, ageing to 64-80°). Found C, 33.0; H, 2.9. C<sub>7</sub>H<sub>8</sub>F<sub>6</sub>O<sub>3</sub> requires C, 33.1; H, 3.2%.

Comparative recrystallisation from wet and dry solvents showed no correlation between production of higher melting range forms and water content of the solvents. Using a dry box recrystallisations were performed from anhydrous solvents at an atmospheric relative humidity of 14%, but both higher and lower range melting forms were obtained, which did not correlate with atmospheric humidity.

Material of m. range 96-98 changed spontaneously at room temperature to give in 13 days a melting range of 75-95° and over a longer period 64-79° melting range material was obtained. Thermal ageing accelerated this process; material of m. range 95-96° was aged at 45° with the following results; after 1 day m. range 87-95°, 5 days 78-92°, 6 days 64-78°, 7 days 65-73°. Repeated experiments showed that the 96-98° melting material yielded 64-79° melting material on heating at 45° for 6-7 days. Once 96-98° range material had yielded 64-79° range melting material by this method it was not possible to regenerate 96-98° range melting material by recrystallisation.

HDPD (melting range 90-95°) was shaken for 7 days and compared with a control experiment where material was merely stored for 7 days. M. range of shaken material 77-80°, control material m. range 85-88°, suggesting vibration accelerated the ageing process.

HDPD (m. range 96-98°) was compared with the normal form (m. range 64-79°) using X-ray crystallography (rotating crystal method and Cu K $\alpha$  radiation). Sieving 96-98° range melting material to get it into the instrument tube produced the 64-79° range form and a method was devised for sticking crystals on the outside of the specimen tube. After photography the m. range of 96-98°C material had changed to 78-82°, perhaps due to a temperature rise, or the effect of X-rays. All forms are crystalline (monoclinic), the difference between higher m. range materials and the 64-79° range melting form is that the higher melting forms produce photographs having pronounced asterism. Control experiments on nickel powder showed this was not due to the instrument. The normal interpretation of asterism is that the material is strained, producing lattice distortion.

#### Acknowledgements

Thanks are due to Professor J.C. Tatlow, Birmingham University for his supervision of this work, to Dr. J.M. Burdon for many helpful conversations, and for n.m.r. analyses and to Birmingham University Analytical Section for elemental analyses.

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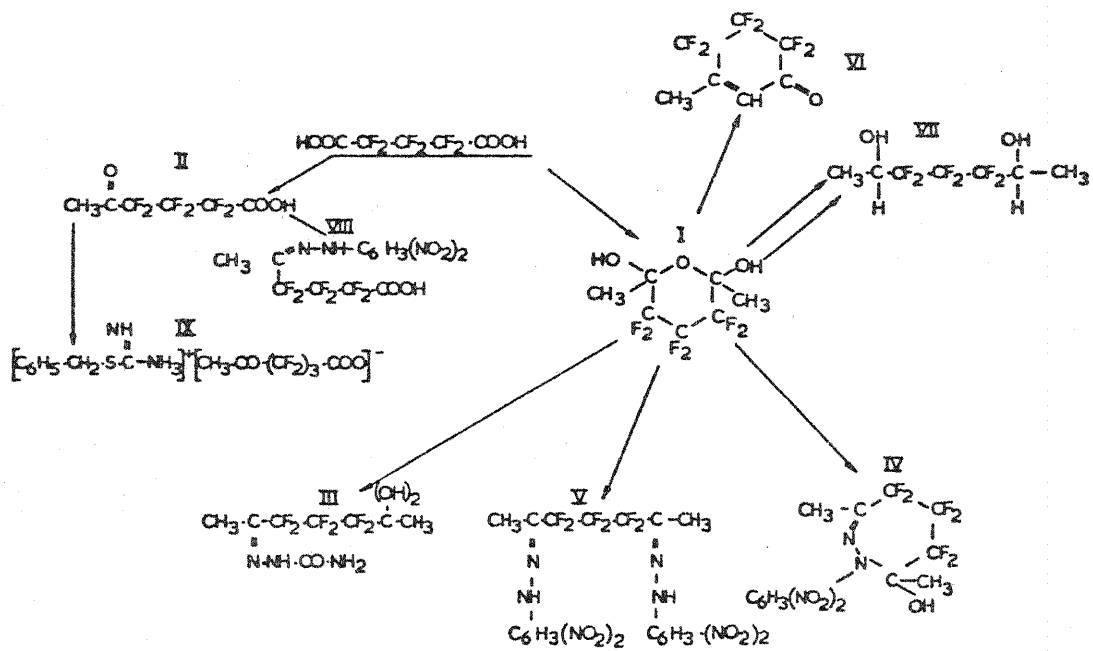


FIG. 1. SOME REACTIONS OF PERFLUORO-GLUTARIC ACID.

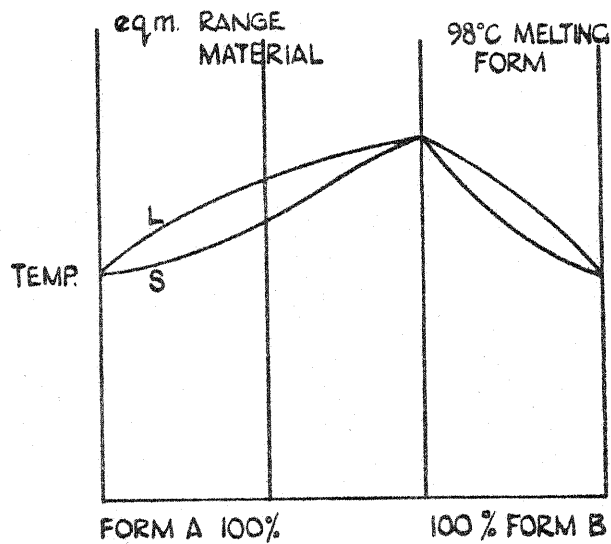


FIG. 2. PHASE DIAGRAM FOR HEXAFLUORO-2,6-DIMETHYLPYRAN-2,6-DIOL.