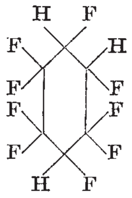
LETTERS TO THE EDITORS

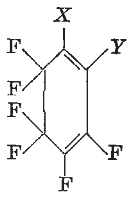
The Editors do not hold themselves responsible for opinions expressed by their correspondents. No notice is taken of anonymous communications.

Hexafluorobenzene

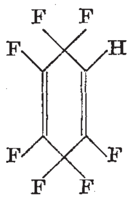
THE application of gas–liquid partition chromatography to organic fluorine chemistry[1,2] has enabled us to extend our studies on dehydrofluorination to a nonafluoro*cyclo*hexane (I) (b.p. 92°) which has been obtained[3,4] by passage of benzene vapour over cobaltic fluoride at about 150°. With concentrated aqueous potassium hydroxide, this polyfluoride (I) gave a complex mixture (b.p. 60–90°) which was shown by analytical gas-chromatography to contain nine individual components. These were separated by use of the preparative-scale gas chromatographic column, and the structures of some of them have been determined by spectroscopic examination, oxidative degradation, addition reactions, etc.



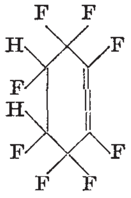
(I)



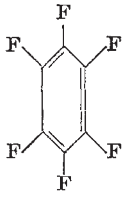
(II) X=H, Y=F
(III) X=F, Y=H



(IV)



(V)



(VI)

Two heptafluoro*cyclo*hexa-1 : 3-dienes (II) (III), a heptafluoro*cyclo*hexa-1 : 4-diene (IV), and an octafluoro*cyclo*hexene (V) were thereby identified. Also, as one of the major products, the important fluorocarbon hexafluorobenzene (VI) was isolated and characterized. The great value of the gas-chromatographic technique in effecting the separations, on a relatively small scale, of complex mixtures such as this is readily apparent. Hexafluorobenzene was prepared in amounts sufficient to carry out a preliminary study, and we have shown that chlorine will add to the ring system to give hexachlorohexafluoro*cyclo*hexane, and that attack by nucleophilic reagents is relatively easy. Thus, with methanolic sodium methoxide, pentafluoroanisole and a tetrafluorodimethoxybenzene were given. These reactions are being actively pursued at present, for a wide field of investigation has been opened up.

The nonafluoro*cyclo*hexane precursor is shown by the products II–VI to be a 1H : 2H : 4H-compound (I). The isolation of hexafluorobenzene upon dehydrofluorination suggests that the hydrogens on carbons 1 and 2 are both axial. Since *trans*-elimination of hydrogen fluoride between these two >CHF groups cannot then occur, the more difficult 'outwards' elimination, with fluorine being lost from the —CF_2— groups, can operate. Similar conclusions apply to the 1H : 2H-decafluoro*cyclo*hexanes, where the *cis*-compound gives exclusively 1H-nonafluoro*cyclo*hexene on dehydrofluorination[5], but the *trans* gives, besides this, some octafluoro*cyclo*hexa-1 : 3-diene[4].

Hexafluorobenzene has been reported before. McBee, Lindgren and Ligett[6] made it from hexachlorobenzene; their product was probably slightly impure and no reactions were given. Désirant[7] claimed to have obtained it by pyrolysis of tribromofluoromethane; but no experimental details were reported.

Experimental. 1H : 2H : 4H-*Nonafluoro*cyclo*hexane*. Benzene was passed in the vapour phase over cobaltic fluoride in a stirred reaction vessel at 150°. The reactor and the conditions described earlier[3] have been improved[4] to give increased yields of polyfluorides with no benzene remaining. Further fractionation, controlled by gas-phase chromatography, of the material having b.p. > 87° gave 1H : 2H : 4H-*nonafluoro*cyclo*hexane*, b.p. 92·0–92·5°, m.p. 44–46°, n^{45} 1·3016 (found: C, 29·2; H, 1·2. $C_6H_3F_9$ requires C, 29·3; H, 1·2 per cent). Yields were 10–15 per cent of the original polyfluoride mixture.

Hexafluorobenzene. The trihydro-compound (50 gm.), potassium hydroxide (85 gm.) and water (250 c.c.) were refluxed together until analytical gas-chromatographic examination showed a large peak due to the desired compound (17 hr.). The organic layer was separated, dried (magnesium sulphate), distilled, and subjected to gas-chromatographic separation. The hexafluorobenzene (5·0 gm.) had b.p. 80°, n_D^{15} 1·3746 (found: C, 38·6; F, 62·0. Calc. for C_6F_6: C, 38·7; F, 61·3 per cent). McBee *et al.*[6] gave b.p. 81–82°, n_D^{20} 1·3760, and Désirant[7] b.p. 80·5°, n_D^{20} 1·3777. Infra-red spectroscopic measurements (on the pure liquid) showed three bands at 1,702, 1,761 and 1,802 cm.$^{-1}$. A band was found in the ultra-violet at λ 2300 A., ε approx. 770 with an inflexion at λ 2500–2550 A. (*c*, 0·11 gm./l. in ethyl alcohol).

Reactions of hexafluorobenzene. (*a*) *Chlorine addition.* Chlorine (1·2 gm.) and the compound (1·0 gm.) were sealed together in a hard glass tube which was irradiated with ultra-violet light for 48 hr. The product was washed (aqueous sodium metabisulphite), dried (P_2O_5) and distilled to give *hexachlorohexafluoro*cyclo*hexane* (1·24 gm.), b.p. 137°/30 mm., m.p. 101–102° (found: F, 28·8. $C_6Cl_6F_6$ requires F, 28·6 per cent). This compound showed no absorption in the infra-red due to unsaturation over the range 1,890–1,580 cm.$^{-1}$.

(*b*) *Action of sodium methoxide.* Hexafluorobenzene (4·8 gm.) was refluxed with methanolic sodium methoxide (40 c.c.; 1 *N*) for 1 hr. The mixture was poured into water and the product extracted with ether. The extracts were washed, dried (magnesium sulphate), and evaporated and the residue distilled to give two fractions: (i) b.p. 145–160° (2·9 gm.) and (ii) b.p. 160–180° (0·7 gm.). Fraction (i) was redistilled to give *pentafluoroanisole*, b.p. 155–157°, n_D^{15} 1·417 (found: C, 42·5; H, 1·8. $C_7H_3F_5O$ requires C, 42·4; H, 1·5 per cent). Fraction (ii) on being kept deposited crystals which were recrystallized from aqueous ethanol to give a *tetrafluorodimethoxybenzene* (0·15 gm.), m.p. 51·5–52·5° (found: C, 46·0;

H, 3·1. $C_8H_6O_2F_4$ requires C, 45·7; H, 2·9 per cent).

J. A. Godsell
M. Stacey
J. C. Tatlow

Chemistry Department,
University, Edgbaston,
Birmingham 15.

June 22.

[1] Evans, D. E. M., and Tatlow, J. C., *J. Chem. Soc.*, 1184 (1955).

[2] Evans, D. E. M., and Tatlow, J. C., Symposium on Vapour Phase Chromatography (Hydrocarbon Research Group, Institute of Petroleum), May–June 1956, Preprints of papers, p. S198.

[3] Barbour, A. K., Mackenzie, H. D., Stacey, M., and Tatlow, J. C., *J. App. Chem.*, **4**, 347 (1954).

[4] Smith, R. P., and Tatlow, J. C. (forthcoming publication).

[5] Roylance, J., Tatlow, J. C., and Worthington, R. E., *J. Chem. Soc.*, 4426 (1954).

[6] McBee, E. T., Lindgren, V. V., and Ligett, W. B., *Indust. Eng. Chem.*, **39**, 378 (1947).

[7] Désirant, Y., *Bull. Classe. Sci. Acad. Roy. Belg.*, **41**, 759 (1955).

Organophilic Montmorillonite Gels

Infra-red absorbance measurements on hydrocarbon gels of dimethyl dioctadecyl ammonium montmorillonite[1] indicate that polymeric-type hydrogen bonding is significant in systems containing this clay mineral derivative. For example, Fig. 1 shows free hydroxyl and bonded hydroxyl absorbances in the 3-micron region for a 20 per cent dispersion of dimethyl dioctadecyl ammonium montmorillonite in a mixture containing 75 per cent cumene and 25 per cent cetane.

We suggest as one possible gelation mechanism that water, present in small amounts in the organophilic clay, forms bridges which hold montmorillonite platelets together, causing a network that leads to gel formation. This explanation appears to account for the unusual properties of these systems. Thus, they are affected by dehydration and, after standing in a desiccator, they are converted by working from gels to viscous liquids. If they are then put into another container over water, they recover their gel status as water vapour is absorbed. These gels lose consistency, as working causes montmorillonite platelets to approach parallel positions. This is apparently because bridging through the solvated layer of organic material is more difficult in the tactoid arrangement which results from working.

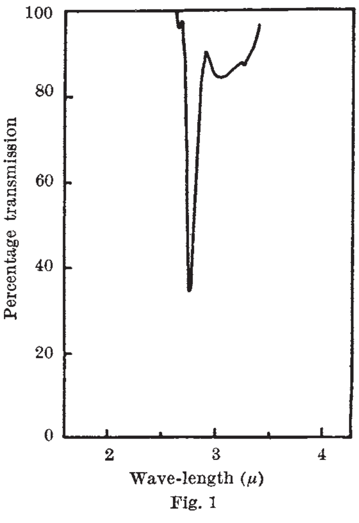


Fig. 1

But the turbulence which accompanies treatment in a sonic generator, colloid mill, paint mill or homogenizer causes platelet edges to force through the solvated layer of other platelets and make bonding contact with the underlying silicate portion of these, thus stiffening the network and explaining the increase in consistency which accompanies such treatment. At high temperatures (>150° C.), a rather firm network can form, apparently because thermal turbulence and loss of solvation in the organic layer permit a closer approach of the inorganic core of particles. This explains the unusual effect observed, that a system in the viscous liquid state changes to a gel when heated. Less water is required for network formation at these higher temperatures, and possibly no water at all, since the approach of the inorganic parts of different platelets may be so close that attractive forces between aluminium ions at the edges of the octahedral layers and negative spots on the faces of other platelets may be large enough to account for network formation.

V. R. Damerell
E. Milberger

Western Reserve University,
Cleveland, Ohio.

[1] Damerell, V. R., *Indust. and Eng. Chem.*, **48**, 321 (1956).

An Ambiguity in the Variable-Solvent Solubility Test: Homogeneity of β_1-Lactoglobulin

In the variable-solvent solubility test (see, for example, Falconer and Taylor[1], Derrien[2], Smithies[3]) a constant amount of protein is brought to a series of different concentrations of a salt, the volume, *p*H and temperature being constant. The equilibrium concentration of protein remaining in solution is then plotted against the concentration of salt. A single protein is expected to give a curve like that in Fig. 1. Here *AB* represents the exponential solubility relationship of the protein[4]. Under conditions represented by the horizontal part *PQ* of the curve (the position of which depends on the amount of protein and

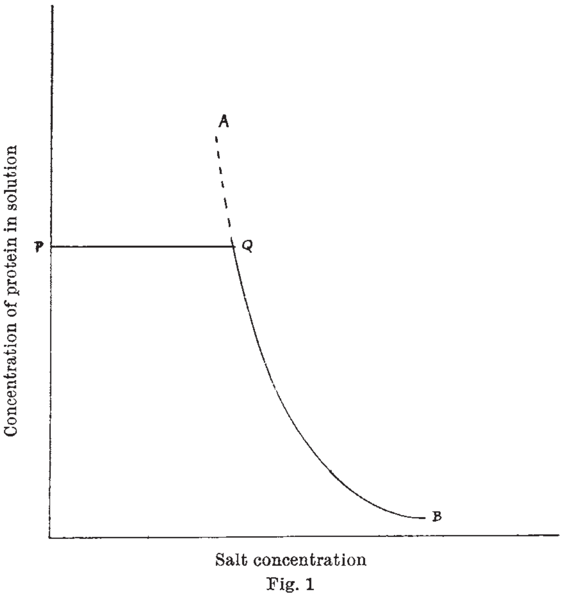


Fig. 1