Tetrahedron. Vol. 31, pp. 1649 to 1651. Pergamon Press 1975. Printed in Great Britain

VALENCE-BOND ISOMER CHEMISTRY—IX[1]

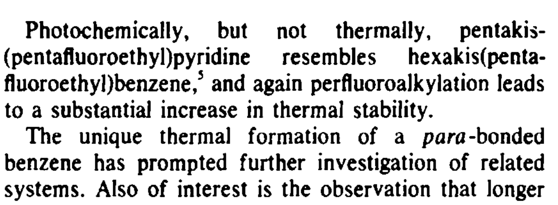
THERMAL AND PHOTOCHEMICAL FORMATION OF VALENCE-BOND ISOMERS OF PERFLUORO-PENTAETHYLMETHYLBENZENE AND -1,2,3,5-TETRAETHYL-4,6-DIMETHYLBENZENE

M. G. Barlow, R. N. Haszeldine* and M. J. Kershaw
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

(*Received in the UK* 19 *February* 1975; *Accepted for publication* 28 *February* 1975)

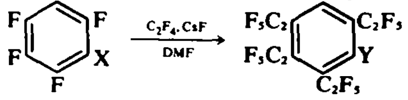
Abstract—Perfluoropentaethylmethylbenzene is thermally (425–600°) or photochemically ($\lambda > 270$ nm) isomerised to a mixture of perfluoro - 1,2,3,5,6 - pentaethyl - 4 - methyl - and possibly perfluoro - 1,2,3,4,5 - pentaethyl - 6 - methyl - bicyclo[2.2.0]hexa - 2,5 - dienes. Perfluoropentaethylmethyltetracyclo[$2.2.0^{2,6}.0^{3,5}$]hexane is formed when shorter wavelength light ($\lambda > 200$ nm) is used. Similarly, perfluoro - 1,2,3,5 - tetraethyl - 4,6 - dimethylbenzene is thermally isomerised (500°) to a mixture of perfluoro - 1,2,3,5 - tetraethyl - 4,6 - dimethyl - and possibly perfluoro - 1,2,4,6 - tetraethyl - 3,5 - dimethylbicyclo [2.2.0]hexa - 2,5 - dienes. The valence-bond isomers have notable thermal stability.

Perfluoroalkylation leads to a notable increase in stability of valence-bond isomers of aromatic compounds. Hexakis(trifluoromethyl)benzene may be readily isomerised by UV light to its benzvalene ($\lambda > 270$ nm), *para*-bonded benzene and prismane ($\lambda > 200$ nm) isomers,[2] and these isomers appear to owe their stability, at least in part, to destabilisation of the parent benzene as a result of severe non-bonding interactions between the alkyl groups.[3] In hexakis(pentafluoroethyl)benzene, steric crowding is even more severe, which is reflected in the UV spectrum, and its *para*-bonded isomer, which may be formed photochemically[2] or thermally,[4] appears to be more stable at high temperatures. Its prismane isomer is readily formed photochemically.



Photochemically, but not thermally, pentakis-(pentafluoroethyl)pyridine resembles hexakis(pentafluoroethyl)benzene,[5] and again perfluoroalkylation leads to a substantial increase in thermal stability.

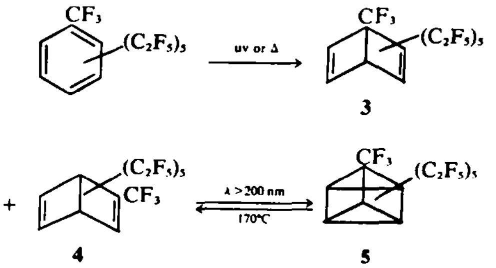
The unique thermal formation of a *para*-bonded benzene has prompted further investigation of related systems. Also of interest is the observation that longer wavelength UV light causes benzvalene formation for the trifluoromethyl-system and *para*-bonded benzene formation, possibly a vibrationally excited ground-state reaction, for the pentafluoroethyl-system. Nucleophilic displacement of fluoride in perfluoroaromatic compounds by perfluorocarbanions, from fluoro-olefins and caesium fluoride in aprotic solvents, provides a convenient route to perfluoroalkyl-derivatives,[6] and perfluoro - pentaethylmethyl - (**1**) and 1,2,3,5 - tetraethyl - 4,6 - dimethyl-benzene (**2**), have been prepared, albeit in low yield, from perfluoro-toluene[7] and -*m*-xylene, respectively:



(X = F or CF_3)

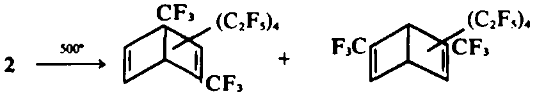
(**1**: Y = C_2F_5, 15%, or **2**: CF_3, 3%)

The UV spectrum of methyl-benzene (**1**), with λ_{max} 204 and 277 nm and prominent inflexion at 213–221 nm, more nearly resembles that of hexakis (pentafluoroethyl)benzene,[2] while that of dimethylbenzene (**2**), with λ_{max} 217 and 282 nm resembles more that of hexakis((trifluoromethyl)benzene with λ_{max} 212 and 283 nm.[2] Presumably this reflects decreasing steric strain. Thermally and photochemically, perfluoro-pentaethylmethylbenzene (**1**) resembles hexakis-(pentafluoroethyl)benzene:



Formation of hexadiene (**3**), isolated by fractional crystallisation, is strongly favoured both photochemically and thermally. The identity of hexadiene (**4**) remains tentative, since attempts to isolate it were unsuccessful, and is based upon the following grounds. UV light converts a mixture of hexadienes (**3** and **4**) to prismane (**5**) in essentially quantitative yield; in turn heating (**5**) yields (**3**) and (**4**). The ^{19}F NMR spectrum of a mixture of hexadienes (3 and 4) shows absorption band systems,† in addition to those due to (3), at 2·2 and 2·6 ($CF_3{\cdot}C{\cdot}C\lessdot$), 5·0 and 7·0 ($CF_3{\cdot}C{\cdot}C$), and 26·9 ppm ($CF_2{\cdot}C\lessdot$), in the expected regions, the remaining bands probably being masked by those of the major component (3).

In a similar manner, dimethyl–benzene (2) isomerised thermally to hexadienes (6) and possibly (7), in the ratio 20:1:



6 7

Unfortunately, the limited amount of benzene (2) available, prevented a study of its photochemistry.

The valence-bond isomers (3) to (6) all have high thermal stability, comparable with those of previously reported perfluoro–alkyl derivatives. Severe non-bonded interactions in the parent benzenes, which are largely relieved in the non-planar valence-bond isomers, appear responsible for both this enhanced kinetic stability, and for the thermodynamic stability of bicyclo[2.2.0]hexa-2,5- dienes, with four or more pentafluoroethyl groups, at high temperatures.

EXPERIMENTAL

Experimental techniques were similar to those described previously.[2,5] Perfluoro–toluene and -*m*-xylene were prepared by the defluorination of the corresponding perfluoromethylcyclohexanes.[8]

Preparation of perfluoroalkylbenzenes

(a) *Perfluoropentaethylmethylbenzene.* A method similar to that previously described was used.[7] Perfluorotoluene (7·5 g, 32·3 mmol), tetrafluoroethylene (20·0 g, 200 mmol), and caesium fluoride (2 g) in DMF (25 ml), sealed in a stainless steel autoclave (250 ml), were shaken at 120° for 19 hr, when the pressure had fallen from 30 to 6 atm. The autoclave was cooled, vented, the remaining dark-brown liquid was poured into water, and the resulting creamy-white solid was separated, washed with cold diethyl ether (4 ml), sublimed at 160°/1 mmHg, and recrystallised from hexafluorobenzene to give perfluoropentaethylmethylbenzene (3·50 g, 4·77 mmol, 15% based upon toluene taken) (Found: C, 27·8; F, 72·1; *M*, 736. Calc. for $C_{17}F_{28}$: C, 27·7; F, 72·3%, *M*, 736), λ_{max} (hexane) 204 (ϵ 18400) and 277 (310), λ_{infl} 213–221 (6800–9100), λ_{min} 254 nm (193), as a white solid, m.p. 158–159°.

The ^{19}F NMR spectrum of the benzene (20% w/v in hexafluorobenzene) showed absorption band systems at −25·3 (3F, CF_3-aryl), −6·0 (15F, $CF_3{\cdot}CF_2$), and 5·7 ppm (10F, CF_2).

(b) *Perfluoro - 1,2,3,5 - tetraethyl - 4,6 - dimethylbenzene.* Perfluoro - *m* - xylene (11·8 g, 41·4 mmol), tetrafluoroethylene (30·0 g, 300 mmol), and caesium fluoride (1 g) in DMF (25 ml), sealed in a stainless steel autoclave, were shaken at 130° for 2 hr. The autoclave was cooled, vented, and the remaining dark-red liquid was poured into water. The reaction was repeated and the combined products were separated, washed with water (2 × 10 ml), dried ($MgSO_4$), and reduced to half-bulk by prolonged evacuation at 30° *in vacuo*, when the remaining dark-red liquid deposited white crystals at 0°. These were recrystallised from diethyl ether to give *perfluoro - 1,2,3,5 - tetraethyl - 4,6 - dimethylbenzene* (1·10 g, 1·6 mmol, 3% based on xylene taken) (Found: C, 28·2; F, 71·5; *M*, 686. $C_{16}F_{26}$ requires: C, 28·0; F, 72·0%; *M*, 686), λ_{max} (hexane) 217 (ϵ 11000), 282 (156), λ_{min} 251 nm (<30), as a white solid, m.p. 112–114°.

The ^{19}F NMR spectrum of the benzene (20% w/v in hexafluorobenzene) showed absorption band systems at −26·0 (4,6-CF_3), −5·7 (1,2,3,5-CF_3), and 5·6 ppm (CF_2).

The perfluoropentaethylmethylbenzene valence-bond isomer system

(a) *UV irradiation of perfluoropentaethylmethylbenzene in perfluoro-n-pentane.* The title benzene (1; 0·776 g, 1·05 mmol) in perfluoro-n-pentane (2·871 g), sealed in a 15 ml silica ampoule, was irradiated at a distance of 25 cm from the lamp for 3 months. The solvent was removed *in vacuo* and the remaining white solid was sublimed at 40°/1 mmHg to give *perfluoro - pentaethylmethyltetracyclo*[2.2.0.0^{2,6}.0^{3,5}]*hexane* (5; 0·568 g, 0·77 mmol, 98% based upon benzene converted) (Found: C, 27·7; F, 71·8; *M*, 736. $C_{17}F_{28}$ requires: C, 27·7; F, 72·3%; *M*, 736), no absorptions at higher frequency than ν_{max} 1419 cm^{-1}, as a white waxy solid, m.p. 117·5–119°. The title benzene (0·194 g, 0·26 mmol, 25% recovery) remained from the sublimation.

A similar reaction in which the benzene (0·445 g, 0·64 mmol) in perfluoro-n-pentane (5·548 g), sealed in a 10 ml silica ampoule, was irradiated for 2 months at a distance of 20 cm from the lamp, which was surrounded by a 1 mm Pyrex filter, gave, after removal of solvent *in vacuo*, a white solid mixture, shown by ^{19}F NMR spectroscopy to comprise unchanged benzene (0·086 g, 0·12 mmol, 19% recovery), perfluoro-1,2,3,5,6-pentaethyl-4-methylbicyclo-[2.2.0]hexa-2,5-diene (0·216 g, 0·29 mmol, 56% based upon benzene converted) (3) (see below), perfluoro - 1,2,3,4,5 - pentaethyl - 6 - methylbicyclo[2.2.0]hexa - 2,5 - diene (0·086 g, 0·12 mmol, 23%; 4), and the above prismane (5; 0·048 g, 0·06 mmol, 12%).

The ^{19}F NMR spectrum of 5 (30% soln in C_6F_6) showed absorption band systems at −15·9 (4-CF_3), +4·2 (3,5-CF_3), 5·0 (1,2,6-CF_3) and 33·9 ppm (CF_2's).

(b) *UV irradiation of solid perfluoropentaethylmethylbenzene.* The title benzene (0·187 g, 0·25 mmol), sealed in a 2 ml silica ampoule, was irradiated for 4 months, when fractional sublimation yielded 5 (0·054 g, 0·07 mmol, 90% based upon benzene converted) and recovered benzene (0·126 g, 0·17 mmol, 70%).

(c) *Thermal isomerisation of perfluoropentaethylmethylbenzene.* The benzene (0·514 g, 0·69 mmol), passed through a silica tube (120 × 1 cm i.d.) heated to 425 ± 5°, gave product, collected at the exit of the tube at −196°, which was fractionally sublimed to give a mixture, shown by ^{19}F NMR spectroscopy to comprise 3 (0·360 g, 0·49 mmol, 80% yielded based upon benzene converted) and 4 (0·050 g, 0·07 mmol, 11%), which sublimed at 25–30°/1 mmHg, and recovered benzene (0·066 g, 0·09 mmol, 13%), which sublimed at 100–120°/1 mmHg.

A similar reaction, in which the benzene was passed through a packed silica tube at 600 ± 10°, gave a mixture of 3 (64% yield), 4 (6%), and benzene (14% recovery).

Attempts to separate the hexadienes by GLC were unsuccessful.

The combined hexadiene fractions were recrystallised twice from dichloromethane and benzene (1:1) at 0° to give *perfluoro - 1,2,3,5,6 - pentaethyl - 4 - methylbicyclo*[2.2.0]*hexa - 2,5 - diene* (Found: C, 27·7; F, 72·2%; *M*, 736), ν_{max} 1667 m cm^{-1} ($F_5C_2{\cdot}C{:}C{\cdot}C_2F_5$str), as a white low-melting solid, m.p. *ca.* 18°.

The ^{19}F NMR spectrum of 3 (30% soln in C_6F_6) showed absorption band systems at −13·6 (4-CF_3), +1·3 (1-CF_3), 5·9 (2,6-CF_3), 6·1 (3,5-CF_3), 27·9 (1-CF_2), 34·6 (2,6-CF_2), and 35·1 ppm (3,5-CF_2, AB-type multiplet with $\delta_A - \delta_B$ = 6·32 ppm, J_{AB} 300 Hz).

(d) *UV irradiation of perfluoropentaethylmethylbicyclo*-[2.2.0]*hexa - 2,5 - dienes.* A mixture of 3 (0·111 g, 0·15 mmol) and 4 (0·011 g, 0·02 mmol) in perfluoro-n-pentane (0·841 g), sealed in a 5 ml silica ampoule, was irradiated for 45 d when the solvent was removed *in vacuo* to leave 5 (0·119 g, 0·16 mmol, 98%), m.p. 116–118°.

(c) *Thermal isomerisation of perfluoro - 1,2,3,5,6 pentaethylmethylbicyclo*[2.2.0]*hexa - 2,5 - diene.* A soln of the title hexadiene (0·117 g) in hexafluorobenzene (1·401 g) was divided into six equal portions which were sealed in small (*ca.* 0·6 ml) soda-glass ampoules. The ampoules were heated (172·5 ± 0·3°) and periodically one was removed and the contents analysed by GLC

---

†To high field of external CF_3CO_2H.

(7 m TXP at 150°C), which indicated aromatisation by first-order kinetics with a half-life of 70 ± 3 hr.

(f) *Thermal rearrangement of perfluoro-pentaethylmethyltetracyclo*$[2.2.0.0^{2,6}0^{3,5}]$*hexane.* The title prismane (0·075 g, 0·102 mmol) and hexafluorobenzene (0·403 g), sealed in an NMR tube, were heated at 172·5 ± 0·3°. Periodic examination by ^{19}F NMR spectroscopy (at 35°) indicated isomerisation, with a half-life of 16 ± 0·6 hr, to **3** and **4**, in the ratio 5:1 after 30·3 hr and benzene (**1**). The amount of benzene formed indicated that **4** aromatised rather more readily than its 4-methyl-isomer.

Thermal isomerisation of perfluoro-1,2,3,5-*tetraethyl*-4,6-*dimethylbenzene*

The title benzene (0·190 g, 0·28 mmol), passed through a silica tube (120 × 1 cm i.d.) packed with silica chips at 500 ± 5°, gave a mixture of a liquid and white solid. The liquid was decanted from the solid and shown by ^{19}F NMR spectroscopy to comprise **6** (0·135 g, 0·20 mmol) and, tentatively, 7 (0·007 g, 0·01 mmol). The solid was shown by IR spectroscopy to be unreacted benzene (0·037 g, 0·05 mmol, 20%).

The mixture of hexadienes was recrystallised from acetone and light petroleum (60–80°) at −25° to give *perfluoro*-1,2,3,5-*tetraethyl*-4,6-*dimethylbicyclo*[2.2.0]*hexa*-2,5-*diene* (0·101 g, 0·15 mmol, 66% yield based upon benzene converted) (Found: C, 27·8; *M*, 686. $C_{16}F_{26}$ requires: C, 28·0%; *M*, 686), ν_{max} 1688 wsh and 1678 m cm^{-1} (C:C str), as a colourless liquid which solidified at *ca.* −10°. The hexadiene, when heated at 250° for 3 hr, was very largely (by IR) isomerised to its parent benzene.

The ^{19}F NMR spectrum of **6** (20% soln in $CFCl_3$) showed absorption band systems at −15·2 (4-CF_3), −14·2 (6-CF_3), +0·9 (1-CF_3), 4·4 (2 or 3-CF_3), 5·0 (3 or 2-CF_3), 5·9 (5-CF_3), 28·0 (1-CF_2), 34·5 (2,3-CF_2), and 37·0 ppm (5-CF_2).

REFERENCES

[1] Part VIII, M. G. Barlow, G. M. Harrison, R. N. Haszeldine, R. Hubbard, M. J. Kershaw and D. R. Woodward, submitted for publication in *J. Chem. Soc.* Perkin I.

[2] M. G. Barlow, R. N. Haszeldine and R. Hubbard, *Ibid.* (C) 1232 (1970).

[3] D. M. Lemal and L. H. Dunlap, *J. Am. Chem. Soc.* **94**, 6562 (1972).

[4] E. D. Clifton, W. T. Flowers and R. N. Haszeldine, *Chem. Commun.* 1216 (1969).

[5] M. G. Barlow, J. G. Dingwall and R. N. Haszeldine, *J. Chem. Soc.* Perkin I 1542 (1973); preliminary communication *Chem. Commun.* 1580 (1970).

[6] R. D. Chambers, J. A. Jackson, W. K. R. Musgrave and R. A. Storey, *J. Chem. Soc.* (C) 2221 (1968).

[7] H. C. Fielding, B.P. 1 076 357/1967.

[8] Part VII, M. G. Barlow, R. N. Haszeldine and M. J. Kershaw, submitted for publication in *J. Chem. Soc.* Perkin I.