para-Bonded Isomers of Fluoroaromatic Compounds

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SYNTHESIS of valence isomers of aromatic compounds has received attention since van Tamelen and Pappas[1] isolated the first authentic bicyclo-[2,2,0]hexa-2,5-diene derivative by photolysis of 1,2,4-tri-t-butylbenzene. The unsubstituted "Dewar benzene" was also prepared by the same authors following a different route.[2] While benzene itself and some of its monosubstituted derivatives are known to undergo irreversible photoisomerization to fulvenes,[3] formation of *para*-bonded intermediates, together with other non-aromatic isomers, has been recently confirmed in the photo-interconversion of polyalkylbenzenes.[4] Similar products have been obtained by the trimerization of t-butylfluoroacetylene.[5]

We describe here the synthesis and some chemical properties of the first perfluoro-derivatives of bicyclo[2,2,0]hexa-2,5-diene to be isolated.

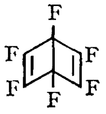
Hexafluorobenzene in the vapour phase and in the presence of an inert gas was irradiated at 20° with light of 2537 Å for 10 hr. to give a mixture of starting material and a perfluoro-olefin (b.p. 52°; *ca.* 60% yield), ν_{max} 1760 cm.$^{-1}$ (–CF=CF–), which was easily separated by fractional distillation. Its ultraviolet spectrum showed only end-absorption. Both mass-spectrometric measurements (top mass peak: 186) and its quantitative conversion into hexafluorobenzene when its vapour was heated at 80° for 4 hr, showed it to be an isomer of the latter. The olefin is apt to explode very violently as a liquid, though it can be stored unchanged in the solid state. Its ^{19}F n.m.r. spectrum,[6] which showed two signals at 122·8 and 191·0 p.p.m., relative to internal CCl_3F, in the ratio of 2 : 1, is of the A_4X_2 type system, consistent with the structure of hexafluorobicyclo[2,2,0]hexa-2,5-diene (I).

The diene (I) reacts with one mole of bromine at room temperature to give 5,6-dibromohexafluorobicyclo[2,2,0]hex-2-ene (b.p. 146°), ν_{max} 1760 cm.$^{-1}$ (–CF=CF–), which can easily be debrominated to the diene (I) and which adds one mole of bromine, in the light, to give the saturated, crystalline tetrabromo-adduct of (I) (m.p. 47·5°, from ethanol–water). This adduct displays a "deceptively simple" A_4X_2 ^{19}F n.m.r. spectrum,[6] with two signals at 118·4 and 141·3 p.p.m., relative to internal CCl_3F, in the ratio 2 : 1.

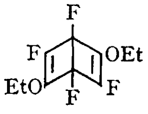
The diene (I) reacts with hydrogen (Pd, 20°) to give a crystalline tetrahydro-adduct (m.p. 90—91°), ν_{max} 3010 cm.$^{-1}$ $(-\overset{|}{\underset{|}{C}}-H)$, and its general reactivity is that of a perfluoro-olefin. Thus it reacts with lithium aluminium hydride to give a complex mixture of products. On treatment with sodium ethoxide two vinylic fluorine atoms are substituted to give an unresolved mixture of the two diethoxy-derivatives (II) and (III), ν_{max} 2990 $(-\overset{|}{\underset{|}{C}}-H)$ and 1710 cm.$^{-1}$ [–CF=C(OEt)–], in the ratio of approximately 2 : 1, as shown by n.m.r. spectroscopy.[6] On heating this product under reflux (*ca.* 195°) for 3 hr. isomerization to a mixture of *para-* and *meta*-diethoxytetrafluorobenzene occurs, as shown by infrared and n.m.r. spectroscopy.[6]

The photo-isomerization was also successfully attempted with octafluorotoluene under the same conditions as described above for hexafluorobenzene. The product (b.p. 62·5°, 20% yield) was easily separated from the starting material by fractional distillation and was quantitatively isomerized to octafluorotoluene, when heated in the vapour phase at 80° for 4 hr. Mass spectrometry shows a top mass peak of 236 and the infrared spectrum, ν_{max} 1762 (–CF=CF–) and 1725 cm.$^{-1}$ [–CF=C(CF$_3$)–], is consistent with a mixture of (IV) and (V) in the ratio of *ca.* 2 : 1, as shown by n.m.r. spectroscopy.[6] The ultraviolet spectrum shows only end-absorption. The mixture was not resolved by gas–liquid chromatography. As a liquid, it is apparently less explosive than the diene (I).

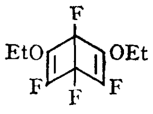
It reacts with one mole of bromine at room temperature. The resulting unresolved dibromo-adducts, ν_{max} 1720 [–CF=C(CF$_3$)–] and 1780 cm.$^{-1}$ (–CF=CF–), do not react with bromine any further, while they can readily be debrominated to the mixture of (IV) and (V).



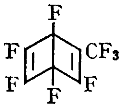
(I)



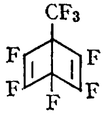
(II)



(III)



(IV)



(V)

Work is in progress to investigate the photochemical behaviour of other aromatic fluorine compounds, as well as to study further reactions of the above-mentioned products.

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