1,3-Cycloaddition Reactions of the *para*-Bonded Valence Isomer of a Substituted Benzene: Hexafluorobicyclo[2,2,0]hexa-2,5-diene as a Dipolarophile, and Phenyl Azide and Diazomethane as Dipoles

By M. G. BARLOW, R. N. HASZELDINE,* and W. D. MORTON

(*Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester* M60 1QD)

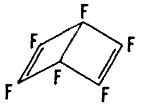
Summary The *para*-bonded valence isomer of hexafluorobenzene is a good dipolarophile and reacts readily with phenyl azide and diazomethane.

THE addition of 1,3-dipoles to double bonds is particularly easy with cyclo-olefins, an effect long attributed to angular strain,[1,2] but is particularly difficult with fluoro-olefins; thus diazoalkanes do not react as 1,3-dipoles with alkenes containing vinylic fluorine,[3] and the reactions of organic azides with perfluoro-olefins require forcing conditions.[4]

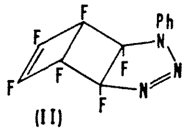
Hexafluorobicyclo[2,2,0]hexa-2,5-diene (I)[5] has now been found to be a reactive dipolarophile, forming, with phenyl azide and diazomethane, novel 1:1 adducts (II and VI), 1:2 adducts (III, VII and VIII), and the aziridine (V), each characterised by elemental analysis, i.r. and n.m.r. spectroscopy, and mass spectrometry. The several adducts are assigned the *exo*-orientation largely on the basis of their ^{19}F n.m.r. spectra (chemical shifts relative to external $CF_3\cdot CO_2H$), and the following observations support this assignment: (i) for the 1:1 adducts (II, VI), and the aziridine (IX), the shifts of the olefinic fluorines, at 42·9 ± 1·2 p.p.m., are substantially invariant, (ii) the bridgehead fluorines, *cis* to the heterocyclic ring, show large and variable shifts from those of the parent bicyclohexadiene (I; at 115·1 p.p.m.), namely (II, 106·3, 114·3; III, 105·3; V, 95·5, 102·7; VI, 103·2, 120·2; VII, 96·3, 118·2; VIII, 107·9; IX, 104·0; and X, 93·1 p.p.m.), and the effect is most pronounced for the compounds which have arisen by reactions involving both double bonds of the parent bicyclohexadiene, (iii) the compounds (II), (III), and (V)—(X) show the number of bands expected on the basis of their symmetry, and (iv) there may be a substantial "through-space" contribution[6] to the cross-ring coupling of the *endo*-fluorines, *e.g.*, the sum of these couplings is *ca.* 45 Hz. in adduct (VIII).

Reaction of the diene (I) with an excess of phenyl azide at 35° gives the 1:1 adduct (II; 42%), m.p. 92°, and when the reaction time is extended the 1:2 adduct (III; 18%) m.p. 118° is obtained, together with the aziridine (V; 21%), m.p. 128° and the 1:1 adduct (II; 19%). The ^{19}F n.m.r. spectrum of the crude product remaining after removal of the 1:1 adduct indicates that the 1:2 adduct (IV; 6%) may also be formed in the reaction, but it was not isolated in a pure state.

Photolysis, in acetone, of the adducts (II) and (V) gives quantitative breakdown to the aziridine (IX; 56%), m.p. 82—83° and the diaziridine (X; 73%), m.p. 119—124° respectively.



(I)



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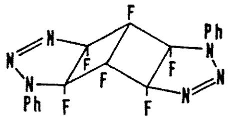

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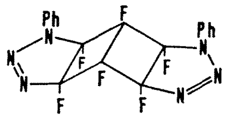
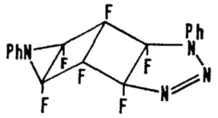
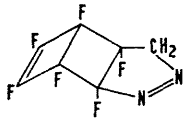


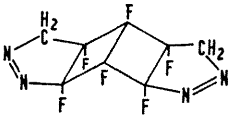
(IV)



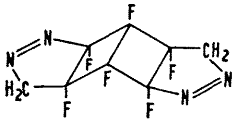
(V)



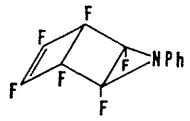
(VI)



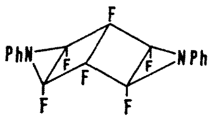
(VII)



(VIII)



(IX)



(X)

Diazomethane reacts rapidly in the dark with an excess of the diene (I) in perfluoropentane at −45° to give the 1:1

adduct (VI; 61%), m.p. 95—97° and a mixture of 1:2 adducts (VII and VIII; 9%), and when an excess of diazomethane is used the products are (VI; 12%), (VII; 38%), m.p. 130°, and (VIII; 38%), m.p. 118° (decomp.).

The use of diazomethane and cuprous ion to generate methylene in the presence of hexamethylbicyclo[2,2,0]hexa-2,5-diene has recently been described and gives the *exo*-mono- and -di-cyclopropyl compounds,[7] but only one 1,3-cycloaddition reaction has been reported hitherto for *para*-bonded valence isomers of aromatic compounds.[8] The ease of the 1,3-cycloaddition reactions when fluorine is a substituent in the olefin is remarkable.

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