Diels–Alder Reactions of the *para*-Bonded Valence Isomer of Hexafluorobenzene and of the Benzvalene Isomer of Hexakis(trifluoromethyl)benzene: Pyrrole as a Diene

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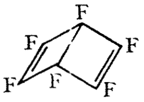
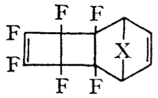
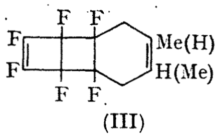
PYRROLE and its derivatives have for long had the reputation of being unsuitable as dienes in the Diels–Alder reaction. Only with *N*-substituted derivatives has any success been achieved; Diels–Alder adducts of *N*-benzyl-, *N*-carboxymethyl-, *N*-triphenylmethyl-, or *N*-1-naphthyl-pyrrole with acetylenedicarboxylic ester in particular have been reported, but the reactions usually involve vigorous conditions and much by-product formation.[1] The reaction of a fluoro-olefin with a diene, if it occurs at all, usually gives a vinylcyclobutane rather than a cyclohexene.


(I)


(II) X = CH_2, O, NH, C:CMe_2, $[CH_2]_2$.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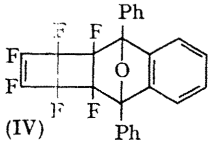
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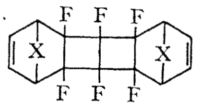
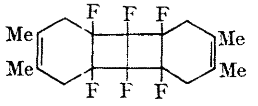

(V) X = CH_2, O, NH, C:CMe_2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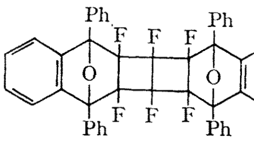
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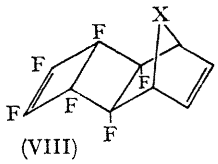
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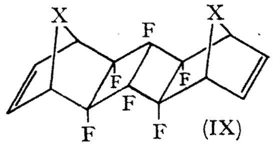
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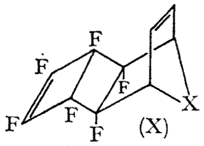
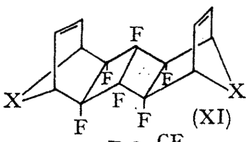

(X)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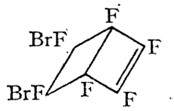
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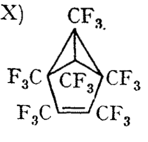
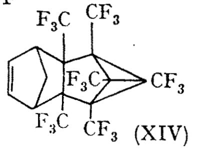

(XIII)


(XIV)

We find that hexafluorobicyclo[2,2,0]hexa-2,5-diene (I)[2] is a reactive dienophile, forming, with a variety of cyclic and acyclic dienes, both 1 : 1 adducts (II), (III), and (IV) and, more slowly, 1 : 2 adducts (V), (VI), and (VII) at ambient temperatures and in 50—95% combined yield. For example the 1 : 1 adduct (II; X = CH_2; 76%) and the 1 : 2 adduct (V; X = CH_2; 17%) are formed in 12 hr. at room temperature (hexafluorobenzene solution) with 94% conversion of the dienophile. Re-aromatisation of (I) is negligible in reactions carried out at room temperature. The reaction times vary from several hours for the most reactive dienes to several months for the least reactive. Dienophile (I) reacts slowly with pyrrole to yield the first examples of Diels–Alder adducts of this heterocycle; thus a 3 : 1 mixture of pyrrole and (I) in ether yields the 1 : 1 adduct (II; $X = \rangle NH$; 58%) and the 1 : 2 adduct (V; $X = \rangle NH$; 5%). The following order of diene reactivity towards dienophile (I) has been observed: 1,3-diphenylisobenzofuran $\simeq$ cyclopentadiene > furan $\geqslant$ αα-dimethylfulvene > 2,3-dimethylbuta-1,3-diene > pyrrole $\geqslant$ 2-methylbuta-1,3-diene > buta-1,3-diene $\geqslant$ cyclohexadiene.

The adducts (II)—(VII) have been characterised by elemental analysis and i.r., n.m.r., and mass spectrometry. An examination of the trends of ^{19}F chemical shifts for the several adducts (II) and (V) suggests that they have the configurations (VIII) and (IX) respectively, rather than (X) and (XI).

The reactivity of (I) as a dienophile is associated particularly with the fused-ring structure, since whilst the *cis-exo*-dibromide (XII) is also a good dienophile under comparable conditions, perfluorocyclobutene is not, even under more forcing conditions.

The benzvalene valence-bond isomer of hexakis(trifluoromethyl)benzene (XIII)[3] is also a very reactive dienophile: cyclopentadiene gives a quantitative yield of the 1 : 1-adduct (XIV) (2 min., 20°).

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[1] L. Mandell and W. A. Blanchard, *J. Amer. Chem. Soc.*, 1957, **79**, 2343, 6198; R. M. Acheson and J. M. Vernon, *J. Chem. Soc.*, 1962, 1148; R. M. Acheson and J. M. Vernon, *J. Chem. Soc.*, 1961, 457; N. W. Gabel, *J. Org. Chem.*, 1962, **27**, 301; L. Mandell, J. V. Piper, and C. E. Pesterfield, *J. Org. Chem.*, 1963, **28**, 574.

[2] C. Camaggi, F. Gozzo, and G. Cevidalli, *Chem. Comm.*, 1966, 313; I. Haller, *J. Amer. Chem. Soc.*, 1966, **88**, 2070.

[3] M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *Chem. Comm.*, 1969, 202.