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Diels–Alder Reactions of Perfluorobicyclo[2.2.0]hex-1(4)-ene with Aromatics

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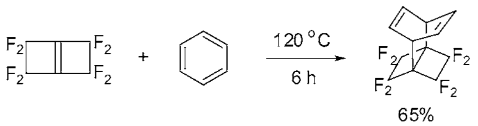
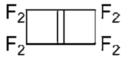
ABSTRACT



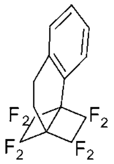
The title perfluoroalkene cycloadds to a variety of aromatic hydrocarbons, including benzene. It is the first alkene to yield a Diels–Alder adduct with benzene and is thus among the most potent dienophiles known.

The highly strained and electron-deficient alkene perfluorobicyclo[2.2.0]hex-1(4)-ene (**1**) is a versatile addend in cycloaddition reactions.[2,3] To explore the limits of its ability as a dienophile, we have investigated its reactivity toward a sampling of aromatic molecules.



1

Alkene **1** reacted with styrene at room temperature to give a mixture containing the adduct **2**. This compound must arise via isomerization of Diels−Alder adduct **3**, which forms at the expense of benzene conjugation. Disruption of the benzene ring under such mild conditions suggested that **1** might be capable of Diels−Alder addition to aromatic systems that resist all but the most potent dienophiles. In contrast to its very labile hydrocarbon parent that dimerizes and polymerizes rapidly at subambient temperatures,[4] alkene **1** is thermally very robust. Thus, its cycloaddition chemistry can be studied at elevated temperatures.



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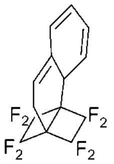

3

No reaction occurred when a solution of **1** and naphthalene in dry acetonitrile was heated at 70 °C for 5 h. Since the loss of conjugation energy accompanying adduct formation should be significantly less in the naphthalene than in the styrene reaction, this result suggests that the latter transformation, at least, occurs stepwise. Generation of a benzylic radical or cation from styrene would leave the benzene ring intact in what could be the rate-determining step. Calculations indicate that corresponding intermediates in the reaction with naphthalene (which may instead be concerted) would lie at higher energies.[5,6]

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(5) Relative to the respective starting materials, the radical resulting from hydrogen atom attack at the α position of naphthalene lies 14.3 kcal/mol above that from attack at the β position of styrene at the HF/6-31G*//3-21G level of theory (0 K, uncorrected for ΔE_{zpt}); for the corresponding cations, the difference is 10.6 kcal/mol. (*Spartan*: Hehre, W.; Wavefunction, Inc.: 188401 Von Karman, Suite 370, Irvine, CA 92717.)

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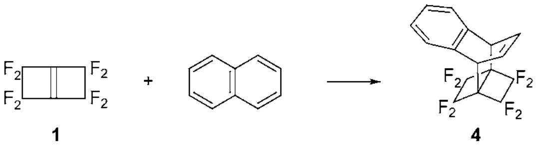
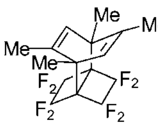
When neat alkene and 3 equiv of naphthalene were sealed in a Pyrex tube and heated for 4 h at 120 °C, all of the alkene was transformed into adduct **4**, isolated in 89% yield (eq 1).



(Eq 1)

We were thus emboldened to attempt reaction with an electron-rich benzene derivative and chose durene. With the same molar ratio of reactants and the same conditions, reaction of the alkene with durene was complete in 5 h.



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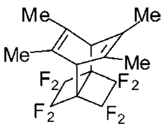
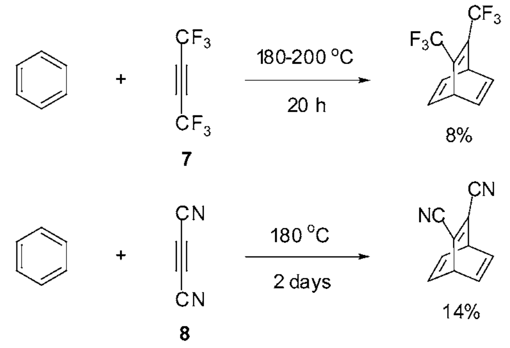


6

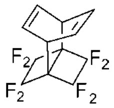
A 2.1:1 mixture of adducts **5** and **6** was obtained in a combined yield of ~80%, as judged from the ^{19}F NMR spectrum. Separation of the adducts from each other and from excess durene was difficult, but a pure sample of **5** was acquired by a combination of silica gel chromatography and preparative gas chromatography. Its C_2 symmetry was apparent from the ^{19}F NMR spectrum, which comprised two AB quartets, and from the ^{1}H NMR spectrum, which showed two different kinds of methyl but one kind of vinyl proton. This structure was unanticipated because other Diels–Alder reactions with durene as a diene proceed by attack at the unsubstituted positions.[7–10] The "abnormal" regiochemistry of the reaction with **1** is probably the result of greater nonbonded repulsion between methyls and fluorines in the transition state for formation of the C_{2v} adduct as compared with that for the C_2 adduct.

Diels–Alder additions to benzene itself as a diene are rare. Benzynes are sufficiently reactive to accomplish this feat,[7,11,12] but the only stable dienophiles that have been added successfully are bis(trifluoromethyl)acetylene (**7**)[13] and dicyanoacetylene (**8**).[14] In the case of both **7** and **8**, conditions were very vigorous and the yields low (Scheme 1).

Scheme 1



Heating alkene **1** with 5 equiv of benzene at 120 °C for 6 h produced adduct **9**, obtained in 65% yield after silica gel chromatography as colorless crystals, mp 186–7 °C. Thus, **1**, the first alkene to form a Diels–Alder adduct with benzene, clearly ranks among the most powerful dienophiles known.



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Acknowledgment. The authors are grateful to the National Science Foundation for support of this work.

Supporting Information Available: Experimental details and characterization data for the adducts. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) There may also be a greater degree of steric hindrance in the transition state of the naphthalene reaction.

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