Polyfluorobicyclo[2,2,0]hex-2-enes as Dienophiles; the Effect of Substituents on the Double Bond

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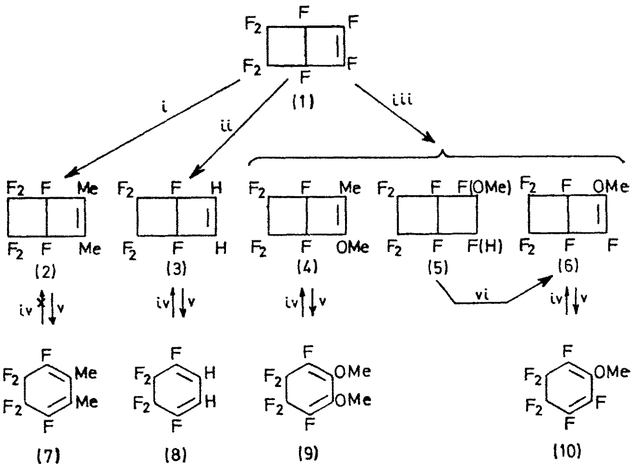
Summary Perfluorobicyclo[2,2,0]hex-2-ene (**1**) is a reactive dienophile and substitution of the vinylic fluorine atoms in (**1**) by hydrogen to give (**3**) increases the dienophilic reactivity towards furan; however, the dimethyl-, monomethoxy-, and dimethoxy-derivatives (**2**), (**6**), and (**4**) display no dienophilic reactivity towards furan.

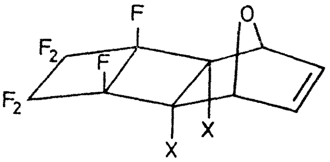
THE dienophilicity of the double bonds in perfluorobicyclo[2,2,0]hexa-2,5-diene has been demonstrated recently.[1] We report that closely related perfluorobicyclo[2,2,0]hex-2-ene (**1**)[2] also shows the expected marked dienophilic character, and that substitution of the vinylic fluorine atoms by other groups has a pronounced effect on this property.

Polyfluorobicyclo[2,2,0]hex-2-enes with substituents on the double bond have been prepared by nucleophilic substitution on (**1**), and in some cases by the photochemical isomerization of the appropriate cyclohexa-1,3-diene, as shown in the Scheme. Moderate yields of the products (**2**)—(**6**) were obtained from reaction of (**1**) with the nucleophiles indicated; however, with the more reactive nucleophilic reagents phenyl-lithium and allylmagnesium bromide only high molecular weight products were obtained and lithium aluminium hydride gave products in which up to five fluorine atoms had been replaced by hydrogen. Photolysis of (**8**) and (**10**), as before,[2] gave good yields of (**3**) and (**6**), but with (**9**) the yield of (**4**) was poor owing to the instability of the diene. Photolysis of (**7**) produced only resin and silicon tetrafluoride. Pyrolyses (**3**) → (**8**) and (**2**) → (**7**) were quantitative at 300° and 10^{-3} mmHg, whereas (**6**) → (**10**) required 400° and 10^{-3} mmHg for complete isomerization. Pyrolysis of (**4**) (400°; 10^{-3} mmHg) gave the new diene (**9**) (*ca.* 90% contaminated with other products). Diene (**9**), obtained pure by preparative gas chromatography, decomposes quickly when left at room temperature.

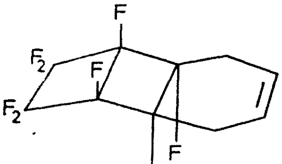


SCHEME. *Reagents*: i, MeLi–Et$_2$O; ii, NaBH$_4$–diglyme; iii, NaOMe–MeOH; iv, *h*ν; v, pyrolysis under reduced pressure; vi, KOH at 170°.
Reaction (v) *and* (vi) *were in flow systems.*

Monoene (**1**) is apparently of similar dienophilic reactivity to perfluorobicyclo[2,2,0]hexa-2,5-diene[1] and gave a 79% yield of adduct (**11**) when a 1:1 mixture of (**1**) with furan was set aside at room temperature for 17 h. Since (**1**) has greater thermal stability than perfluorobicyclo[2,2,0]hexa-2,5-diene it is possible to increase the rate of reaction with less reactive dienes by using elevated temperatures; *e.g.* (**1**) with buta-1,3-diene at 100° for 30 h gave a 67% yield of (**13**).



(11) X = F
(12) X = H



(13)

Replacement of the vinylic fluorines in (**1**) by hydrogen caused a marked increase in dienophilicity towards furan. Olefin (**3**), when set aside overnight at room temperature with furan in carbon tetrachloride, reacted quantitatively to give adduct (**12**). When a mixture of equimolar amounts of (**1**) and (**3**) was treated with furan in carbon tetrachloride at room temperature g.l.c. analysis showed that (**3**) was consumed to the extent of *ca.* 90% after 45 min, whereas less than 5% of (**1**) had reacted.

Substitution of the vinylic fluorines of (**1**) by methyl groups [to give (**2**)] or by one or two methoxy-groups [to give (**6**) and (**4**)] completely destroyed the dienophilicity of the double bond. Thus, olefins (**2**), (**6**), and (**4**) did not react with furan in carbon tetrachloride at room temperature over several weeks. There was no reaction when olefin (**4**) was heated with furan *in vacuo* at 100° for 19 h.

Compounds (**7**),[3] (**8**),[4] and (**10**)[5] had the correct i.r. spectra; all new compounds [*i.e.* (**2**)—(**6**), (**9**), (**11**), (**12**), and (**13**)] were characterized by elemental analysis, mass, i.r., ^1H and ^{19}F n.m.r., and where appropriate u.v. spectroscopy. The stereochemistry of adducts (**11**), (**12**), and (**13**) was assigned as shown in the formulae by analogy with that established for perfluorobicyclo[2,2,0]hexa-2,5-diene adducts.[1] These results and related work will be fully reported in due course.

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