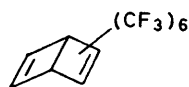


Studies on Organic Fluorine Compounds. Part 26.† Diels–Alder Reaction of Hexakis(trifluoromethyl)bicyclo[2.2.0]hexa-2,5-diene

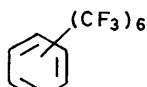
By Yoshiro Kobayashi,* Takaharu Nakano, Ryoji Takahashi, and Itsumaro Kumadaki, Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan

Hexakis(trifluoromethyl)bicyclo[2.2.0]hexa-2,5-diene (1), which had been reported to be unreactive with dienes, was heated with dienes at 140° to give Diels–Alder adducts in good yields. The temperature must be strictly maintained, since starting materials were recovered at lower temperature, and isomerization of (1) occurred at higher temperature. Reaction of (1) with cyclohexa-1,3-diene gave benzene and the 3,4-dihydro isomer of (1) probably through an ene reaction.

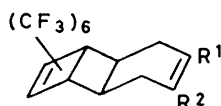
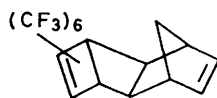
ACCORDING to Haszeldine *et al.*,¹ polyfluorinated bicyclo[2.2.0]hexa-2,5-dienes react as active dienophiles in the Diels–Alder reaction, but hexakis(trifluoromethyl)bicyclo[2.2.0]hexa-2,5-diene (1), the Dewar-type isomer of hexakis(trifluoromethyl)benzene (2), was less reactive



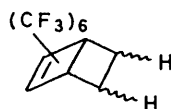
(1)



(2)

(3) R¹ = R² = H(4) R¹ = H, R² = CH₃(5) R¹ = R² = CH₃

(6)



(7)

towards cycloaddition, failing to react with cyclopentadiene or phenyl azide at room temperature. We now report that (1) reacts with various dienes to give Diels–Alder adducts at high temperature without isomerization of (1) to (2).

We recently reported the Diels–Alder reaction of hexakis(trifluoromethyl)benzvalene,² another valence-bond isomer of (2), and Dewar tetrakis(trifluoromethyl)thiophen,³ which were extremely reactive dienophiles. Since (1) has the same structure in the olefinic portion as the benzvalene and the Dewar thiophen, (1) was expected to react with dienes to give the Diels–Alder adducts under more drastic condition. When (1) was treated with butadiene at 140° for six days, the Diels–Alder adduct (3) was obtained in 64% yield, without by-products. The temperature is critical, since if it was too high, (1) isomerized to (2), and if too low, the Diels–Alder reaction did not occur. The results of the Diels–

Alder reaction of (2) with other dienes are summarized in the Table.

Reaction of compound (1) with various dienes

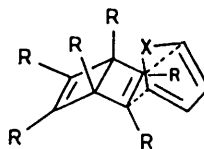
Diene	Product (%)	T/°C	t/days
Butadiene	(3) (64)	140	6
2-Methylbutadiene	(4) (80)	140	5
2,3-Dimethylbutadiene	(5) (76)	140	5
Cyclopentene	(6) (52)	140	10
Cyclohexa-1,3-diene	(7) (100)*	140	2

* Benzene also obtained.

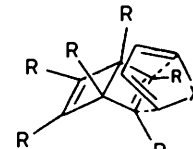
Reaction with cyclohexadiene did not give a Diels–Alder adduct, but compound (7) and benzene were obtained. In this case, an ene reaction seems to have occurred first, followed by elimination of benzene.

Hexa-2,4-diene did not react with (1) probably due to the steric disadvantages of the cisoid form, nor did furan give an adduct. In the latter case, the Diels–Alder reaction seems to be reversible due to the aromatic stability of furan, and isomerization of (1) to (2) predominates.

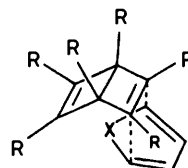
The stereochemistry of the adducts is *exo-anti* by consideration of the steric effects in the transition state for cycloaddition [see (I)–(IV)]; steric effects seems to be minimal for (I).



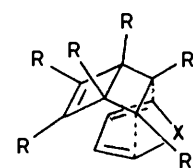
(I)



(II)



(III)



(IV)

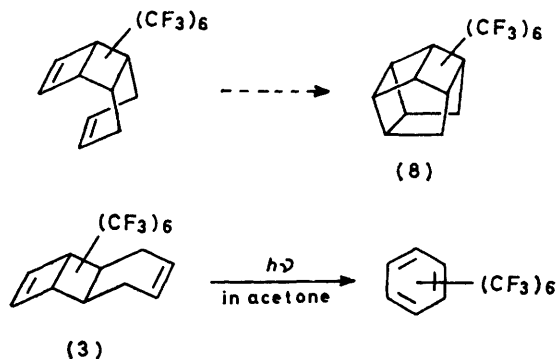
R = CF₃

If *endo*-adducts were formed they should give cage compounds (8) upon u.v. irradiation (Scheme). When

† Part 25, Y. Kobayashi, M. Honda, Y. Hanzawa, I. Kumadaki, and A. Ohsawa, *J.C.S. Perkin I*, 1979, 1743.

(3) was irradiated in acetone by a high-pressure mercury lamp, a cage compound was not obtained, only hexakis(trifluoromethyl)benzene. This also supports an *exo*-structure for the Diels–Alder adducts.

Heszeldine reported¹ that the steric effect of the bridgehead trifluoromethyl groups of (1) inhibited the Diels–Alder reaction, but we have now found that the reaction proceeds under more drastic conditions, although (1) is much less reactive than the corresponding benzvalene.



SCHEME

EXPERIMENTAL

Diels–Alder Reactions of (1).—*With butadiene.* Hexakis(trifluoromethyl)bicyclo[2.2.0]hexa-2,5-diene (1) (500 mg) and butadiene (1.5 ml) in *n*-pentane (5 ml) were sealed in a stainless steel vessel under vacuum, and heated at 140° for 6 days. The ¹⁹F n.m.r. spectrum of the mixture showed that 64% of (1) was converted into the Diels–Alder adduct (3). No other products were observed by ¹⁹F n.m.r. and g.l.c. Solvent was removed on a vacuum line and the residue was recrystallized from *n*-pentane and sublimed at 50° to give 1,2,3,4,5,6-hexakis(trifluoromethyl)tricyclo[4.4.0.0^{2,5}]deca-3,8-diene (3), m.p. 142°; δ_F(CDCl₃; external standard PhCF₃) -4.4 (6 F, s), -2.0 (6 F, s), and 2.0 p.p.m. (6 F, s); δ_H(CDCl₃) 6.12 (2 H, m, =CH) and 2.82 (4 H, m, CH₂); ν_{max}(C₅H₁₂) 1 710 (CF₃C=CCF₃) and 1 180 cm⁻¹ (C–F); *m/e* 540 (*M*⁺) (Found: *M*⁺, 540.019 0. C₁₆H₈F₁₈ requires *M*, 540.018 1).

With 2-methylbutadiene. Compound (1) (50 mg) and 2-methylbutadiene (20 mg) in *n*-pentane (0.1 ml) were sealed in a Pyrex n.m.r. tube under vacuum, and heated at 140° for 5 days. Conversion of (1) into the adduct (4) (80%) was observed by ¹⁹F n.m.r. After removal of the solvent on a vacuum line the residue was recrystallized from *n*-pentane

and sublimed at 50–60° to give adduct (4), m.p. 50°, δ_F(C₅H₁₂) -2.8 (6 F, s), 0.0 (6 F, s), and 2.8 p.p.m. (6 F, s); δ_H(CDCl₃) 5.80br (1 H, s, =CH), 2.74br (4 H, s, CH₂), and 1.88br (3 H, s, CH₃); ν_{max}(C₅H₁₂) 1 710 (CF₃C=CCF₃) and 1 180 cm⁻¹ (C–F); *m/e* 554 (*M*⁺) (Found: *M*⁺, 554.033 4. C₁₇H₈F₁₈ requires *M*, 554.033 8).

With 2,3-dimethylbutadiene. Compound (1) (50 mg) and 2,3-dimethylbutadiene (20 mg) in *n*-pentane (0.1 ml) were treated similarly. The yield of adduct (5) was estimated to be 76% by ¹⁹F n.m.r., m.p. 98–100°; δ_F(C₅H₁₂) -3.6 (6 F, s), -0.3 (6 F, s), and 3.4 p.p.m. (6 F, s); δ_H(CDCl₃) 2.85 (2 H, d, *J*_{gem} 16 Hz, CH₂), 2.60 (2 H, d, *J*_{gem} 16 Hz, CH₂), and 1.79 (6 H, s, CH₃); ν_{max}(C₅H₁₂) 1 710 (CF₃C=CCF₃) and 1 200 cm⁻¹ (C–F); *m/e* 568 (*M*⁺) (Found: *M*⁺, 568.047 2. C₁₈H₁₀F₁₈ requires *M*, 568.047 2).

With cyclopentadiene. Compound (1) (500 mg) and cyclopentadiene (660 mg) in *n*-pentane (5 ml) were sealed in a Pyrex tube under vacuum and heated at 140° for 10 days. After the removal of the solvent on a vacuum line, the residue was recrystallized from *n*-pentane and sublimed at 50° to give 2,3,4,5,6,7-hexakis(trifluoromethyl)tetracyclo[6.2.1.0^{2,7}.0^{3,6}]undeca-4,9-diene (6) (52%), m.p. 88°; δ_F(C₅H₁₂) -4.4 (6 F, s) and -0.6 p.p.m. (12 F, s); δ_H(CDCl₃) 6.48br (2 H, s, =CH), 3.56br (2 H, s, CH), 2.58 (1 H, d, *J*_{gem} 12 Hz, CH₂), and 1.81 (1 H, d, *J*_{gem} 12 Hz, CH₂); ν_{max}(C₅H₁₂) 1 710 (CF₃C=CCF₃) and 1 200 cm⁻¹ (C–F); *m/e* 552 (*M*⁺) (Found: *M*⁺, 552.019 2. C₁₇H₈F₁₈ requires *M*, 552.018 1).

With cyclohexadiene. Compound (1) (70 mg) and cyclohexadiene (48 mg) in *n*-pentane (0.2 ml) were sealed in a Pyrex tube under vacuum, and heated at 140° for 2 days. The reaction mixture were analysed by g.l.c. [DEGS (3 m × 3 mm); 80°]. Two products was detected. The product with the shorter retention time was benzene and the other was hexakis(trifluoromethyl)-5,6-dihydrobicyclo[2.2.0]-hex-2-ene (7) (100%). The dihydro-derivative (7) was separated as an oil by preparative g.l.c. [DEGS (7 m × 10 mm); 80°]; δ_F(C₅H₁₂) 0.4 (6 F, s), 1.6br (6 F, s), and 7.2 (6 F, s); δ_H(CCl₄) 3.95 (2 H, m, -CH); ν_{max}(CCl₄) 1 710 (CF₃C=CCF₃) and 1 200 cm⁻¹ (C–F); *m/e* 488 (*M*⁺) (Found: *M*⁺, 487.983 9. C₁₂H₂F₁₈ requires *M*, 487.986 8).

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