

THE C_4X_4 NETWORK: ISOLATION OF A STABLE ISOMER IN THE PERTRIFLUOROMETHYL SERIES.

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A recent report by Kobayashi and his co-workers¹ on the flash thermolysis of 1,2,3,4,5,6-hexakis(trifluoromethyl)tetracyclo[4.4.0.0.^{2,4}.0^{3,5}]deca-7,9-diene (5a) encourages us to report our own results[†] in this area.

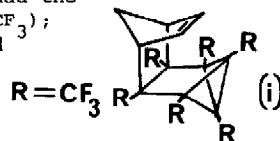
Preparation of the above-mentioned diene (5a) was achieved by an alternative route to that described by the Japanese workers, and involved the steps outlined in Scheme 1. Thus reaction of hexakis(trifluoromethyl)benzvalene^{§2} (1a) with cyclobutadiene (2) (generated from its iron tricarbonyl complex³) in ethanol at 0°, yielded a mixture (52%; ratio 3:2) of two 1:1 adducts⁴ which were separated by glc;[†] the major *syn*-isomer (3a) [¹Hnmr(CDCl₃): δ3.60 (m, cyclobutyl); 6.40 (m, vinylic). ¹⁹Fnmr (acetone, δ_{ext.} CF₃COOH) 25.0 (m, 3F, C3-CF₃); 21.5 (m, 3F, C4-CF₃); 16.25 (m, 6F, C2,5-CF₃); 12.9 (m, 6F, C1,6-CF₃)]. Minor *anti*-isomer (4a) [¹Hnmr(CDCl₃): δ3.75 (t, J_v 1.3Hz, cyclobutyl); 6.40 (m, vinylic). ¹⁹Fnmr (as above): 23.5 (m, 3F, C3-CF₃); 21.5 (m, 3F, C4-CF₃); 15.4 (m, 6F, C2,5-CF₃); 9.4 (m, 6F, C1,6-CF₃)] m/e 538 (M⁺, 31%), 69 (100%). The stereochemical assignment rested on the deshielding of the C3-CF₃ group in the ¹⁹Fnmr of the *syn*-isomer, and the *shielding* of the C1,6-CF₃ groups in the *anti*-isomer by the olefinic centre in each isomer,** and comparison with model compounds.

[†] Taken from the Ph.D. thesis of (E.E.N.) A.N.U. 1972. Presented in part at the Royal Australian Chemical Institute, National Organic Chemistry Conference, Adelaide, May 1972.

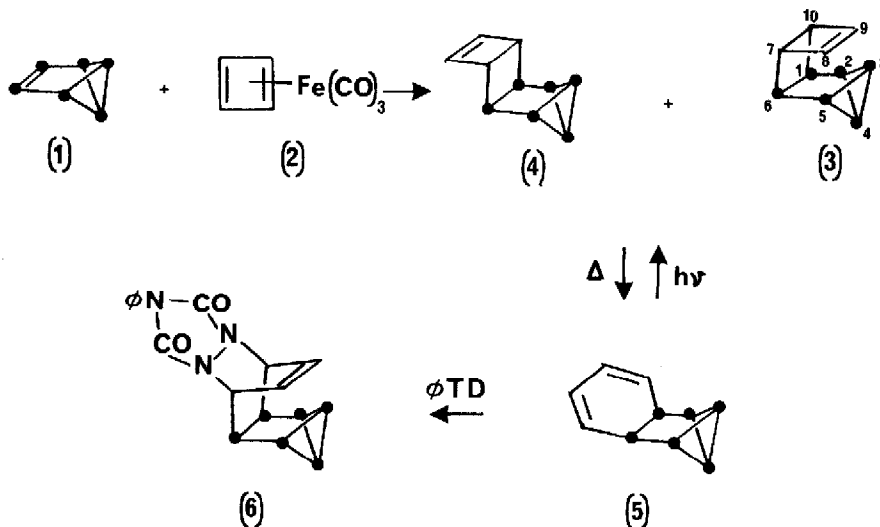
§ This can be obtained essentially free from its valence isomers by irradiation of hexakis(trifluoromethyl)benzene in acetone solution (vycor filter), ca. 32% yield after 16 hr. Unchanged aromatic can be recovered.

‡ 6' x $\frac{3}{8}$ " column, 10% SE30 on Embacel, 70°. Retention times (3a)5.6min; (4a)6.9min; (5a)8.8min.

** Similar reasonings suggested that the cyclopentadiene adduct (i)⁷ had the *endo*-stereochemistry (¹⁹Fnmr: 24.2 (m, 3F, C8-CF₃); 20.8 (m, 3F, C9-CF₃); 15.7 (m, 6F, C7,10-CF₃); 15.5 (m, 6F, C1,6-CF₃); m.p. ca. 250° sealed tube, m/e 552 (M⁺ 63%).



SCHEME 1



For clarity, substituted atoms are designated by a black dot ●.

Compounds (a): CF_3 substituent; compounds (b): H substituent;

compounds (c): F substituent.

Controlled thermal ring-opening ($240^\circ/\text{hr}$) of these adducts yielded the diene (5a).

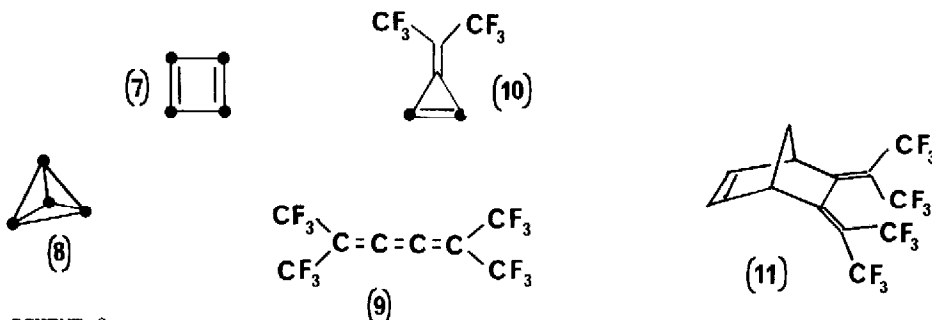
[$^1\text{Hnmr}$: δ 5.9-6.3 (m, H7,10-olefinic); 6.3-6.6 (m, H8,9-olefinic). $^{19}\text{Fnmr}$ (CDCl_3): 23.4 (m, 3F, C3- CF_3); 22.1 (m, 3F, C4- CF_3); 17.1 (m, 6F, C2,5- CF_3); 10.5 (m, 6F, C1,6- CF_3)] m/e 538 (31%), 69 (100%). This compound was characterised as its *N*-phenyltriazolinedione adduct (6a), m.p. $195\text{--}196^\circ$, m/e 713 (M^+ , 24%), 324 (59%), 227 (100%), 214 (54%).

Irradiation of the diene (5a) in ether (vycor filter, 0° , American Hanovia lamp) gave no evidence for fragmentation^{§§}, but yielded a mixture (1:1) of the valence isomers (3a) and (4a)⁸.

Flash vacuum pyrolysis of the diene (5a) at $700^\circ/0.001\text{mm}$, on the other hand, formed substantial quantities of fragmentation products. Our results are in sharp contrast with those reported by Kobayashi and coworkers, since we observed a monomeric $\text{C}_4(\text{CF}_3)_4$ species as the major product, in addition to the dimeric $\text{C}_8(\text{CF}_3)_8$ [cyclobutadiene *anti*-dimer m/e 648 (M^+ 3%),

§§ Compare results reported by G. Maier, *Angew.chem.internat.edit.*, 1974, 13, 425.

629 (100%]], hexafluorobut-2-yne, 1,2-bis(trifluoromethyl)benzene and other fluorine containing products.

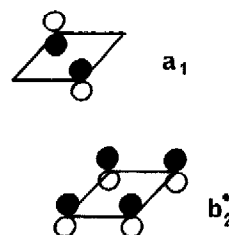


SCHEME 2.

The nature of this monomeric species (see Scheme 2) was of considerable interest since it is the first stable member of this series. This compound was isolated by glc/ms [retention time SE30 column 0^o, 0.7min, m/e 324 (M^+ 40%), 255 (100%)]. The simplicity of the ¹⁹Fnmr (singlet 25.3) is consistent with the cyclobutadiene(7), the tetrahedrane(8), or the cumulene(9) structures; the methylene cyclopropene(10) being ruled out by this evidence. Adduct formation with cyclopentadiene eliminated the tetrahedrane structure. The uv spectrum of this adduct (λ_{max} 234, 279 nm) suggested that it retained significant conjugation, and this, together with the *symmetrical* nature of the ¹⁹Fnmr (two multiplets at 13.5, 13.1) supports the adduct structure(11), which in turn indicates the cumulene structure(9) for the C₄-product. The progenitor of this hexakis (trifluoromethyl) butyatriene remains unidentified.

The $t_{1/2}$ values for thermal ring-opening of the isomers (3a) and (4a) have been found to be 14 min and 3.1 min at 240° respectively. This result is surprising since arguments based on steric strain surely indicate that (3a) should rearrange more readily. Inspection of models suggests that the separation between C₃ and C₈ in the *syn*-isomer (3a) is only 2.5Å. Orbital interactions between the π MO's of the double bond and those of the bicyclobutane ring could modify the stability of (3a)⁹.

The significant interactions are between the π MO of the double bond with both HOMO (a_1) and LUMO (b_2^*) of bicyclobutane. The former interaction is destabilizing and the latter is stabilizing.⁹ In order to ascertain the dominant interaction extended Hückel (EH) calculation on the parent (3b) and hexafluoro (3c) molecules were carried out.¹⁰ The sign of the π -bond order between C₈C₃ (-0.01) and C₈C₅ (-0.007) provides a good indication



of the nature of the interaction.⁹ Thus the overall interaction is a *destabilizing* one.⁹ Introduction of electron withdrawing fluorine atoms had virtually no effect on these bond orders. This destabilizing interaction should manifest itself in a lowering in the activation energy for the ring opening reaction compared with the *anti*-isomer(4a). Thus our results are consistent with theory if our rates were measured at a temperature greater than the isokinetic point. We are pursuing this aspect further.

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9. Sensitised irradiation (acetone) yielded a new isomer. This will be discussed in a forthcoming communication.
10. Similar arguments were first advanced by Jorgensen and Borden: W.L. Jorgensen and W.T. Borden, *J. Amer. Chem. Soc.*, 95, 6649 (1973); W.L. Jorgensen, *ibid.*, 97, 3082 (1975); W.L. Jorgensen and W.T. Borden, *Tetrahedron Lett.*, 223 (1975).
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