

DIELS-ALDER ADDUCT OF HEXAKIS(TRIFLUOROMETHYL)BENZVALENE WITH CYCLOBUTADIENE

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Following the thermolysis of 1,2,3,4,5,6-hexakis(trifluoromethyl)tetracyclo-[4.4.0.0^{2,4}.0^{3,5}]deca-7,9-diene (I)¹⁾, photolysis of I was investigated, since C₄(CF₃)₄ compounds had been expected to be obtained.²⁾ However, irradiation of I with a low pressure mercury lamp gave a mixture (1:1) of two isomers (II and III) of I. The compounds (II and III) were also obtained by the Diels-Alder reaction of hexakis(trifluoromethyl)benzvalene (IV) with cyclobutadiene (V). (Chart 1.) While our work had been in progress, Warrener et al.³⁾ reported that the Diels-Alder reaction of IV with V gave the same products as ours. However, they assigned the structures to these two isomers in the opposite way from ours: the syn-form to the compound showing the same physical property as II (anti-form), and vice versa.

In this report, our results will be discussed first, and the justification of our stereochemical assignment of II and III, with the result of X-ray analysis, will be shown.

The two compounds (II and III) were revealed to be valence-bond isomers of I on the basis of the following properties; II: ¹⁹F-nmr (CCl₄) ppm:⁴⁾ -11.4, -7.8, -2.0, +1.6 (intensity ratio, 1:1:2:2), ¹H-nmr (CCl₄) δ: 3.5 (2H, methine), 6.27 (2H, vinylic), mass spectrum m/e 538 (M⁺). III: ¹⁹F-nmr (CCl₄) ppm -9.4, -7.4, -0.9, +5.4 (intensity ratio, 1:1:2:2), ¹H-nmr (CCl₄) δ: 3.68 (2H, methine) 6.3 (2H, vinylic), mass spectrum m/e: 538 (M⁺). The C3-CF₃

group of the syn-form was expected to be more shielded by the olefinic center than that of the anti-form. Therefore, by comparison of the peak at -11.4 ppm in ^{19}F -nmr of II with that at -9.4 ppm of III, II was tentatively assumed to be the anti-isomer and III, the syn-isomer.

The order of $t_{1/2}$ values for the thermal ring opening of II and III (141 min and 26 min at 207° in diglyme) was in good agreement with the expected one from the steric models of II and III.

To confirm the stereochemistry of II and III, X-ray analysis of the bromides was planned. Both compounds were brominated by bromine in CCl_4 to dibromides (VI and VII): VI; mp $86-87^\circ$ (colorless needles from MeOH); ^1H -nmr (CCl_4) δ : 3.30 (2H, methine), 5.30 (2H, H-C-Br); ^{19}F -nmr (CCl_4) ppm -12.0, -7.8, -2.0, +0.4 (intensity ratio, 1:1:2:2); mass spectrum m/e 677 (M-F). VII: mp $112-112.5^\circ$ (colorless needles from MeOH); ^1H -nmr (CCl_4) δ : 3.48 (2H, methine), 5.16 (2H, H-C-Br); ^{19}F -nmr (CCl_4) ppm -11.2, -7.6, -1.4, +6.2 (intensity ratio, 1:1:2:2); mass spectrum m/e 677 (M-F).

The compound (VII) was used for X-ray analysis. The crystals were grown from a methanol solution as colorless blocks. The lattice constants and intensity data were obtained from the measurements on a Philips PW1100 X-ray diffractometer using $\text{CuK}\alpha$ radiation monochromated by a graphite plate.

Crystal data: $\text{C}_{16}\text{H}_4\text{F}_{18}\text{Br}_2$, M. W. 696. Monoclinic, $\text{P}2_1/\text{n}$, $a=14.948(8)$, $b=14.795(8)$, $c=9.386(4)\text{\AA}$, $\beta=91.39(4)^\circ$. $U=2075\text{\AA}^3$.

The intensities were measured by the θ - 2θ scan method with a scan speed of 6° min^{-1} in 2θ . The scans were repeated twice when the total counts during the single scan was less than 3000. The background was measured at each end of the scan for half the scan time. The size of the crystal was about $0.3 \times 0.1 \times 0.1$ mm and no corrections were applied for absorption. Of the total of 2248 reflexions within 2θ of 100° , 1787 had intensities greater than 2σ (I) level and these were used for the present study. The structure was solved by the heavy atom method using the bromine atoms. The refinement was carried out by the block-matrix least-squares method to an R value of 0.073. At the final stage, the anisotropic thermal vibrations were taken into account for all atoms. Hydrogen atoms were not located in the present analysis. The

weighting system was $\sqrt{w}=0.1$ for $|F_o| < 5$ and $\sqrt{w}=5/|F_o|$ for $|F_o| \geq 5$. Figure 1 shows a stereoscopic view of the molecule drawn by the plotter program ORTEP.⁵⁾ The atoms were drawn by the ellipsoids, each of which encloses 10% of the probability of finding the center of the atom in it.

Therefore, III was determined to be the syn-form and II the anti-form. These results justified the validity of our stereochemical assignment of II and III. Warrener and his co-workers' fallacy is attributable to wrong reasonings concerning the shielding effect due to the olefinic center and the thermal reaction.

Finally, it should be pointed out that cyclobutadiene (V) gave the syn- and anti-adducts with the benzvalene (IV) in equal quantities, since it had been shown that the benzvalene (IV) reacted with usual dienes in the Diels-Alder reaction through an exo transition state because of steric repulsion of the trifluoromethyl group on the bicyclobutane ring of IV.⁶⁾ This might be ascribed to the high reactivity and/or the small steric requirement of IV in the Diels-Alder reaction.

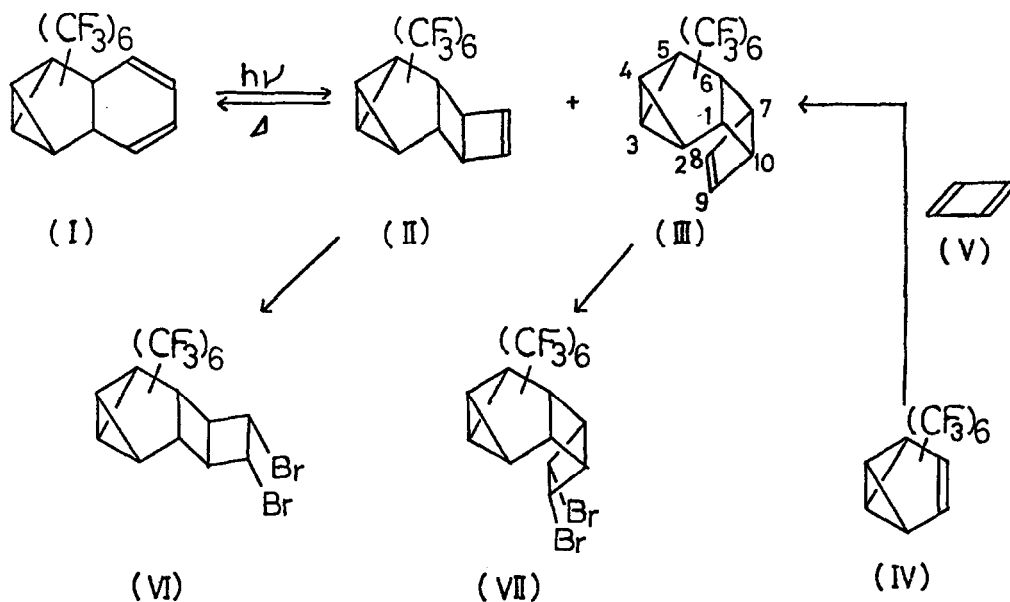


Chart 1

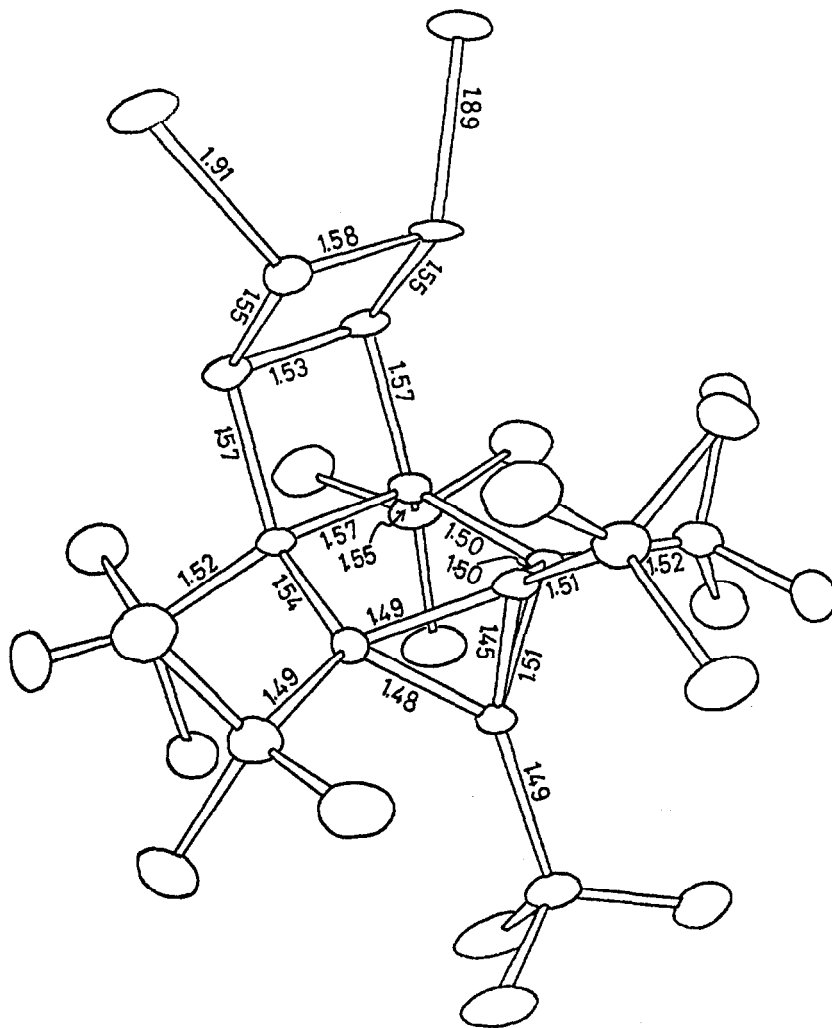


Fig. 1 Bond Length (\AA)

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