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SYNTHESIS AND 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

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Recently[1)] we reported that the ozonolysis of hexakis(trifluoromethyl)benzvalene (I) gave hexakis(trifluoromethyl)benzvalene ozonide (II) and the photolysis of II gave tetrakis(trifluoromethyl)cyclobutadiene-syn-dimer (III) via tetrakis(trifluoromethyl)cyclobutadiene (IV), which is one of the $C_4(CF_3)_4$ units

In this communication, we report the synthesis and 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 (V), which can be a precursor as II of IV.

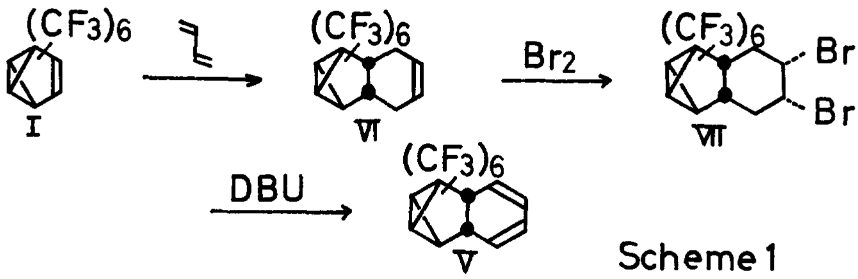
When I was treated with 1,3-butadiene in n-pentane at 90° for 4 hr, a Diels-Alder adduct (VI) was obtained in a quantitative yield, mp 100° (in a sealed tube, colorless needles from n-pentane); mass spectrum m/e 540 (M^+); ir (nujol) 1565 cm^{-1} (cyclopropane), 1240 cm^{-1} (C-F); ^{1}H-nmr (CCl_4) δ 2.50 (2H, d, J = 14.8 Hz), 3.01 (2H, d, J = 14.8 Hz), 6.09 (2H, s); ^{19}F-nmr (CCl_4) ppm[2)] 3.0 (6F, m), -3.2 (6F, m), -8.8 (3F, m), -10.4 (3F, m).

Bromination of VI in carbon tetrachloride at room temperature for 1 day gave dibromide[3)] (VII) in 54.5% yield, mp 68° (in a sealed tube, colorless needles from methanol); mass spectrum m/e 698 (M^+); ir (nujol) 1552 cm^{-1} (cyclopropane), 1240 cm^{-1} (C-F); ^{1}H-nmr (CCl_4) δ 2.43 (2H, m), 3.07 (2H, m), 4.42 (2H, m); ^{19}F-nmr (CCl_4) ppm 1.8 (6F, m), -3.0 (6F, m), -8.4 (3F, m), -12.2 (3F, m).

By dehydrobromination of VII with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in methanol at 90° for 2 hr, V was obtained in 15.6% yield,[4)] mp 210° (in a sealed tube, colorless needles from n-pentane); mass spectrum m/e 538 (M^+); ir (nujol) 1560 cm^{-1} (cyclopropane), 1231 cm^{-1} (C-F); ^{1}H-nmr (CCl_4) δ 6.06 (2H, m), 6.37

(2H, m); ^{19}F-nmr (CCl_4) ppm 3.2 (6F,m), -4.0 (6F, m), -9.6 (3F, m), -11.2 (3F,m)

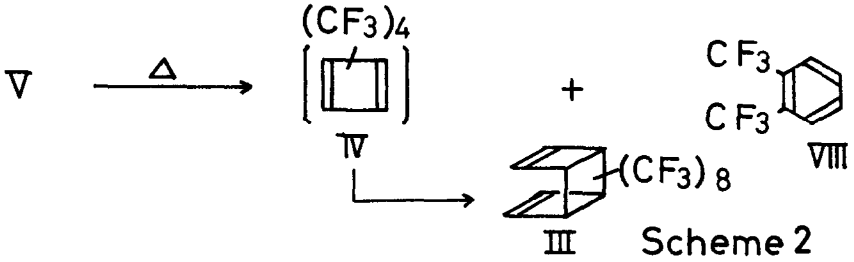
These reactions are summarized in Scheme I.



Scheme 1

In the mass spectrum of V,5) m/e 214 (70) peak corresponding to $C_6H_4(CF_3)_2$ and m/e 324 (47) peak corresponding to $C_4(CF_3)_4$ were observed.

Then we tried the flash thermolysis of V at 490° at 50 mm Hg under nitrogen as a carrier. As major products, III and 1,2-bis(trifluoromethyl)benzene (VIII) were isolated in the yields of 19.4% and 14.7%, respectively.6) In this reaction mixture, tetrakis(trifluoromethyl)cyclobutadiene-anti-dimer was not observed. These facts mean that IV was generated as an intermediate to III in the thermolysis mentioned above.



Scheme 2

The mechanism is under investigation in more detail and that on the minor products of this flash thermolysis is carried on to clarify the reaction path.

REFERENCE AND NOTES

1) Y.Kobayashi, I.Kumadaki, A.Ohsawa, Y.Hanzawa, M.Honda, and Y.Iitaka, Tetrahedron Letters, 1975, 3001.
2) Benztrifluoride: +0 ppm as an internal standard.
3) The bromination of VII was assumed to be cis-addition,as a cis-dibromide, whose structure was determined by X-ray analysis, was obtained as a sole dibromide by the similar bromination of the adduct of I and furan (unpublished)
4) V was isolated using preparative v.p.c.
5) M/e 255 (100) peak corresponding to $C_4(CF_3)_3$.
6) These products were identified with the authentic samples.