

DERIVATION OF OXAHOMOCUBANES FROM DEWAR THIOPHENE¹⁾

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Heicklen and others proposed that the structure of photoisomerization product of tetrakis-(trifluoromethyl)-thiophene (I) is of Dewar type from its ¹⁹F-NMR²⁾, and we also, independently, confirmed the fact from the data of ¹⁹F-NMR and ¹³C-NMR³⁾. However, the reactivity of the Dewar thiophene (II) has never been studied, nor any chemical fact has been reported to support the structure. In this communication, we report the investigation of the reactivity of II in the Diels-Alder reaction with furan derivatives in order to confirm the structure of II and, then, the conversion of the Diels-Alder products to oxahomocubanes.

Compound II reacted with furan (IIIa) in chloroform at room temperature to give an adduct (IVa) [mp 132-133°; NMR ¹H: δ 5.40 (methine-H), 6.61 (olefinic-H), ¹⁹F: δ (from C₆H₅CF₃) -2.50, -2.33; m/e 424 (M⁺)]. As the absorption of $\nu_{\text{CF}_3-\text{C}=\text{C}-\text{CF}_3}$ was not observed in the IR spectrum of IVa, it is certain that the double bond of II underwent the reaction. Further, II reacted with tetramethylfuran (IIIb) in the same manner to give an adduct (IVb) [mp 76°; NMR ¹H: δ 1.77, 1.76 (methyl-H), ¹⁹F: δ -6.92, -4.28; m/e 461 (M-F)]. On the other hand, with 2,5-diethyl-3,4-bis-(trifluoromethyl)-furan (IIIc) the starting material was recovered in the same reaction condition. Since the reaction readily proceeded with IIIb where the substituent is a rather bulky methyl group while IIIc with the electron-withdrawing trifluoromethyl group did not react, the electronic effect of substituents on the furan ring seems to be more important in this reaction than the steric one.

As for the structure of IVa and IVb, it is clear from the above data that they are Diels-Alder-type adducts, but the steric configuration had not been

known yet. Therefore, IVa was desulfurated with triphenylphosphine to give Va [oil; IR: 1718 cm^{-1} ($\nu_{\text{CF}_3-\text{C}=\text{C}-\text{CF}_3}$); m/e 392 (M^+)]. Because the peak of methine-proton shifted from 5.44 to 4.89 and olefinic-proton did not shift in the NMR spectrum of Va, cyclobutene ring is thought to be exo to furan ring, although the configuration of thiirane ring is still uncertain at this stage. IVb was desulfurated in the same manner to give Vb [mp 66° ; NMR ^1H : δ 1.75, 1.57 (methyl-H); ^{19}F : δ -2.16, -0.72; IR 1718 cm^{-1} ($\nu_{\text{CF}_3-\text{C}=\text{C}-\text{CF}_3}$)].

Since the above data are not enough to determine the whole configuration of IV, we performed X-ray analysis of IVb and determined the structure including the configuration of thiirane ring as shown in Chart 1.⁴⁾

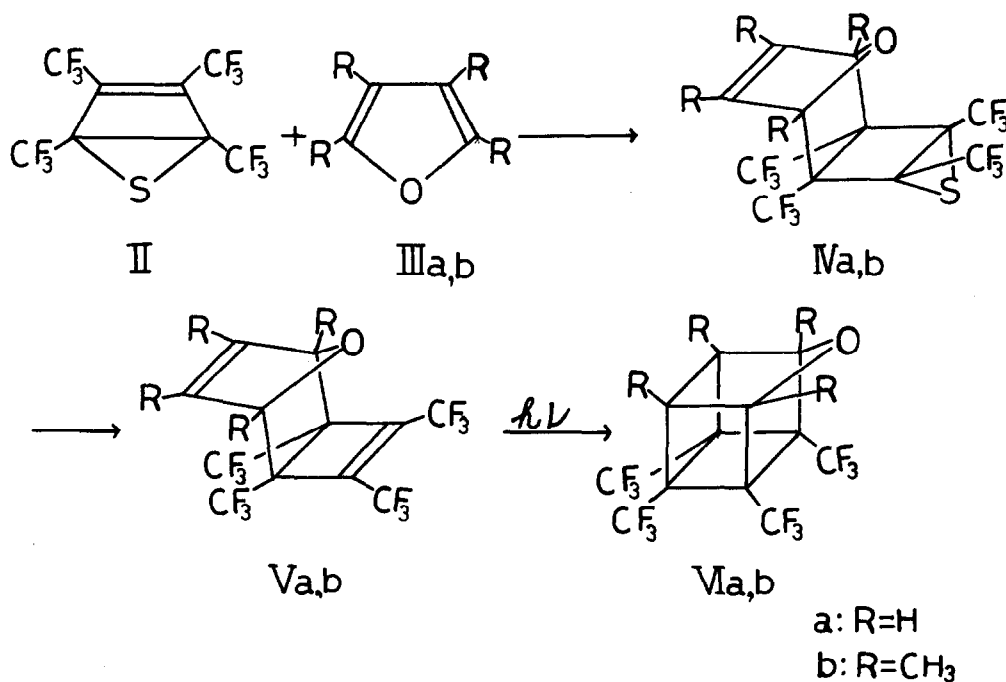


Chart 1

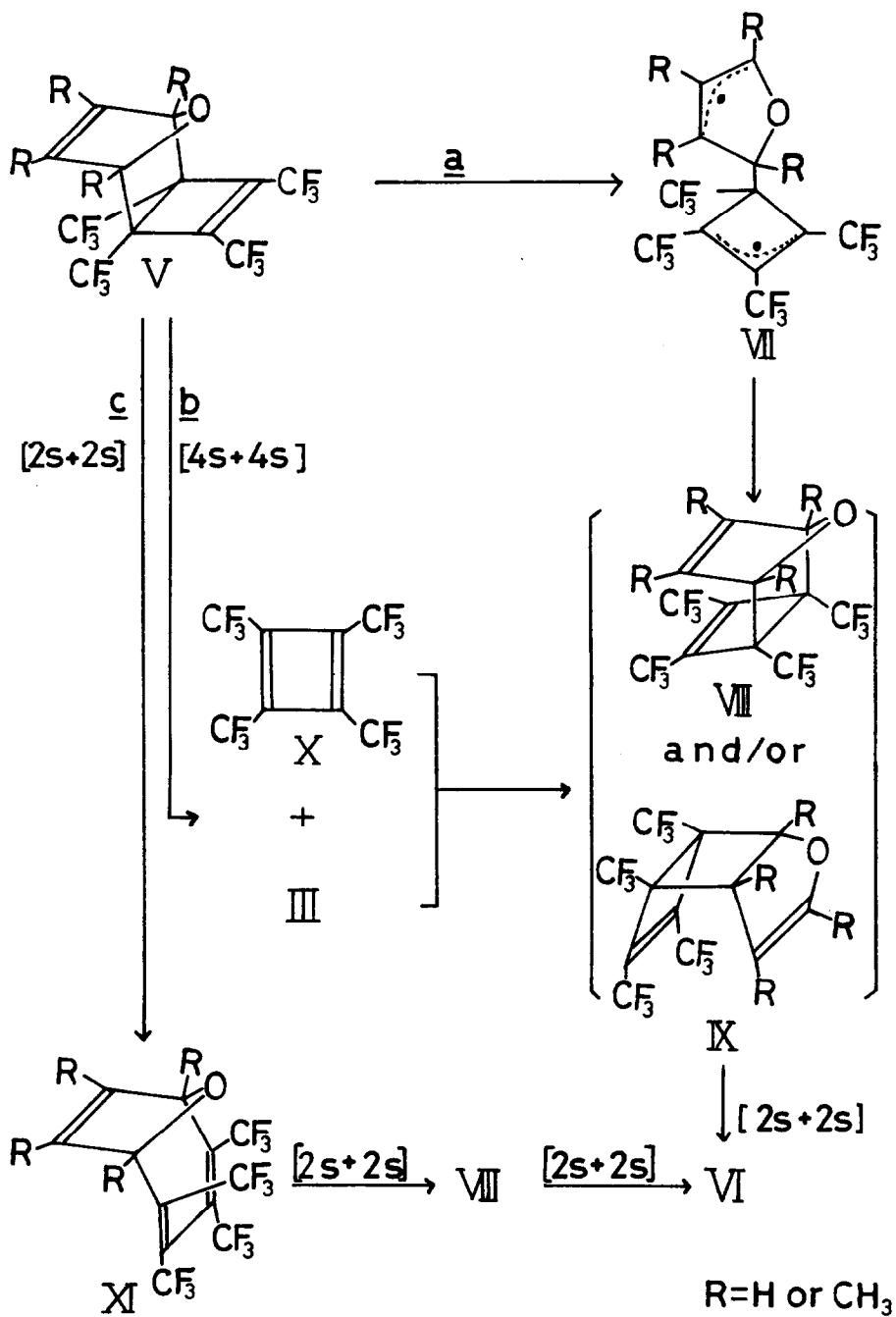
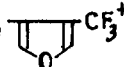
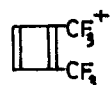
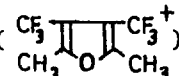



Chart 2

Next, as we considered that oxahomocubane can be derived by isomerizing Va and Vb to endo-type in some way, we irradiated them in acetonitrile with a low-pressure mercury lamp to obtain VIa [mp 156-157°; NMR ^1H : δ 5.64, 3.69; ^{19}F : δ 3.75, 7.60 (intensity ratio 1:1); m/e 392 (M^+), 204 (CF_3 ) CF_3^+), 188 (CF_3 ) CF_3^+)] and VIb [mp 205°; NMR ^1H : δ 1.63, 1.21; ^{19}F : δ 0.00, 3.44 (intensity ratio 1:1); m/e 448 (M^+), 232 (CF_3 ) CF_3^+), 216 (CH_3 ) CH_3^+]]. The structure of VI is confirmed to be oxahomocubane from the above data, especially the fission pattern in the mass spectrum. The results are shown in Chart 1. The structure of II is, therefore, chemically proved to be of Dewar type. Among the above reaction processes, that from V to VI is of special interest from the mechanistic viewpoint. The possible mechanisms that we could think of are shown in Chart 2: a) one which proceeds via biradical (VII)⁵, b) one where the ring closes again after III and X were produced by retro-Diels-Alder reaction, and c) one where XI is first produced in photoreaction by ring-opening following the formula of 2s + 2s and afterwards closes. The mechanism b) or c) may be the case, since the reaction was not disturbed in the presence of 1,3-pentadiene, which is a triplet scavenger.

References and Notes

- 1) A part of this communication was presented at the 6th Symposium on Heterocyclic Compounds, November 1973, Nagoya.
- 2) H.A. Wiebe, S. Braslavsky, and J. Heicklen, *Can. J. Chem.*, **50**, 2721 (1972).
- 3) Presented at the 93rd Annual Meeting of the Pharmaceutical Society of Japan, April 1973, Tokyo. Abstract, p. 146.
- 4) Another paper in regard to this part of the work in collaboration with Y. Iitaka and others will be published later.
- 5) W. Eberbach and M. Perround-Arguëlles, *Chem. Ber.*, **105**, 3078 (1972).