Tetrahedron Letters No. 12, pp 1019 - 1022, 1978. Pergamon Press. Printed in Great Britain.

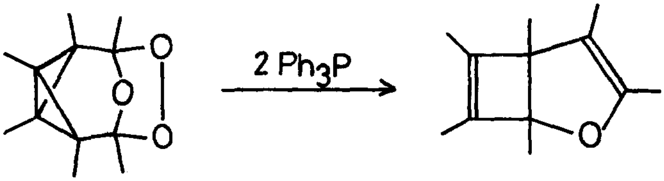
CONVERSION OF A VALENCE-BOND ISOMER OF HEXAKIS(TRIFLUOROMETHYL)OXEPIN TO TETRAKIS(TRIFLUOROMETHYL)FURAN

Yoshiro Kobayashi,* Yuji Hanzawa, Yasuo Nakanishi, and Takashi Kashiwagi
Tokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo 192-03, Japan

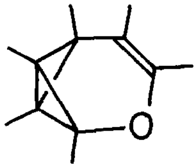
(Received in Japan 7 December 1977; received in UK for publication 6 January 1978)

We have reported the synthesis of two valence-bond isomers of hexakis(trifluoromethyl)oxepin by the reaction of hexakis(trifluoromethyl)benzvalene ozonide with triphenylphosphine.1) We now wish to report the thermal and cycloaddition reactions of hexakis(trifluoromethyl)oxepin isomers and the formation of tetrakis(trifluoromethyl)furan.

Hexakis(trifluoromethyl)-2-oxabicyclo[3.2.0]heptadiene (I) and hexakis(trifluoromethyl)-3-oxatricyclo[4.1.0.0^{2,7}]heptene (II), which are valence-bond isomers of hexakis(trifluoromethyl)oxepin, are stable compounds at room temperature.



(I)



(II)

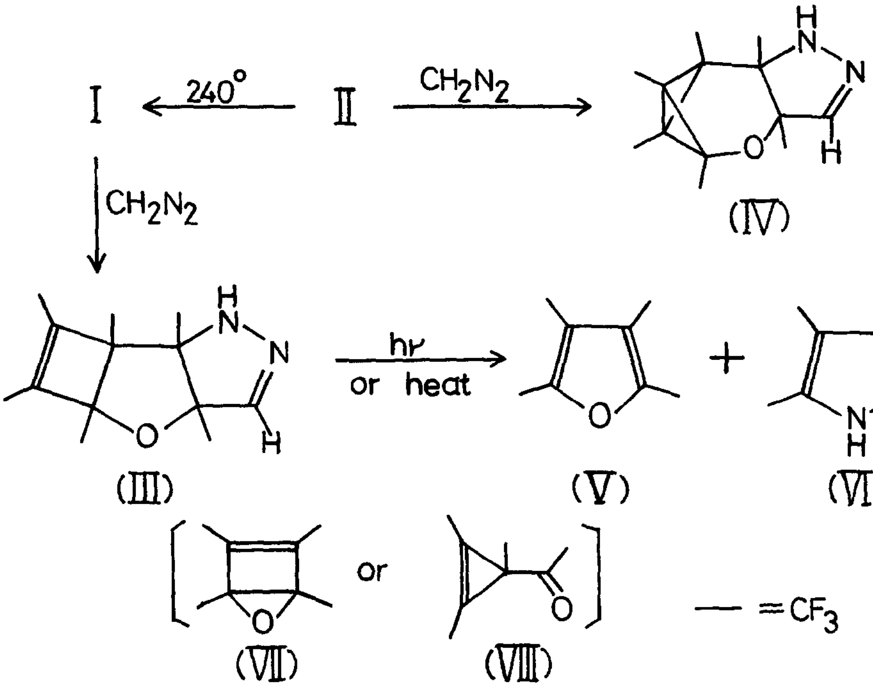
When these isomers were heated at 240°, only the isomer (II) was converted to I quantitatively and no change was observed for I at this temperature. Thermolysis of I at a more elevated temperature (330-350°) only gave rise to decomposition and the hexakis(trifluoromethyl)oxepin could not be obtained as a product.2)

Reactivity of the olefin part of the isomers (I and II) was found to be very low. Diels-Alder adducts of I and II could not be obtained when the cyclic dienes and butadiene derivatives were used as a diene component at 25-100°. These results are highly contradictory to the Diels-Alder reactivity of hexakis(trifluoromethyl)benzvalene3) and hexakis(trifluoromethyl)-Dewar benzene,4) because these two isomers of hexakis(trifluoromethyl)benzene afford Diels-Alder adducts in a relatively good yield.

Although the Diels-Alder adducts of I and II could not be obtained, 1,3-dipolar cycloadducts of I and II with diazomethane, which easily reacts with hexakis(trifluoromethyl)benzvalene to give a 1,3-dipolar cycloadduct,5) were obtained smoothly at room temperature. In the case of I, the adduct (III) was obtained in 86.9% yield.6) In the IR spectrum, this adduct (III) shows no absorption at around 1680 cm^{-1} due to the enol-ether double bond. Therefore, the 1,3-dipolar cycloaddition of I with diazomethane is considered to proceed at the side of enol-ether double bond. III [colorless crystals, mp 78-79°; ir cm^{-1} (Nujol); 3250 (ν N-H), 1700 (cyclobutene double bond); ^{19}F-nmr (Et_2O) ppm7); -9.48, -2.4, +2.8, +3.52, +8.16 (relative intensity ratio, 1:1:2:1:1); mass spectrum m/e 544 (M^+), 340, 204]. From these data, the structure of III was suggested to be 1,3,4,5,6,7-hexakis(trifluoromethyl)-8,9-diaza-2-oxatricyclo[5.3.0.$0^{3,6}$]deca-4,9-diene. In the case of II, the adduct (IV) was also obtained quantitatively.8)

The regioselectivity of the addition reaction of diazomethane to the enol-ether double bond was surmised on the basis of the theoretical analysis by Fukui and his co-workers.9)

Thermolysis of III without any solvent at 140° for 1 hr gave tetrakis-(trifluoromethyl)furan (V) and 4,5-bis(trifluoromethyl)pyrazole (VI), in respective yields of 78.5% and 92.8%.



The compound VI was identified with an authentic sample[10] by comparison of ir spectra and by a mixed melting point determination.

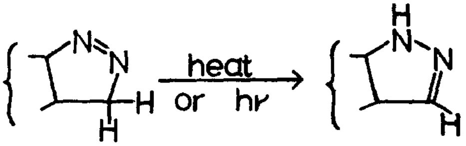
V is a volatile liquid and is separable from VI using a vacuum line; [V; ir cm^{-1} (CCl_4); 1640, 1450, 1150-1290 (ν C-F), 980; ^{19}F-nmr (perfluoropentane) ppm, -4, +1.6 (equal intensity); mass spectrum, *m/e* 340 (M^+)].

V is the first example of tetrakis(perfluoroalkylated)furan.[11] Formation of V and VI was also neatly achieved by direct and/or sensitized irradiation of III.[12] The reaction process of photo- and thermal reaction was considered to proceed through a Dewar type of furan (VII) or a cyclopropenyl derivative (VIII). No change was observed with IV under the same reactions as with III.

The photoreaction of the obtained furan (V) did not give any isomerized products. Moreover, no Diels-Alder adducts of V with dienophiles were obtained. Stability of the furan compound (V) to irradiation under any conditions is greatly different from the results with tetrakis(trifluoromethyl)thiophene[13] and tetrakis(trifluoromethyl)pyrrole.[14]

References and Notes

1) Y. Kobayashi, Y. Hanzawa, and Y. Nakanishi, Tetrahedron Lett., 3371 (1977).
2) We are investigating the flash thermolysis of I at 500-600°.
3) Y. Kobayashi, I. Kumadaki, A. Ohsawa, Y. Hanzawa, M. Honda, Y. Iitaka, and T. Date, Tetrahedron Lett., 2545 (1976).
4) Y. Kobayashi, and T. Nakano, unpublished data.
5) M. Honda, Doctoral Dessertation, Tokyo College of Pharmacy, 1977.
6) The primary 1,3-dipolar cycloadduct was observed in ^{19}F-nmr spectrum, but we did not isolate the primary adduct. The primary adduct isomerizes easily to III, by heating or by irradiation as follows:



7) Benzotrifluoride signal is used as an internal standard; upfield shifts are quoted as positive.
8) Structure of IV was considered to be 1,3,4,5,6,7-hexakis(trifluoromethyl)-8,9-diaza-2-oxatetracyclo[5.3.0.0^{3,5}.0^{4,6}]dec-9-ene (IV) from the ^{19}F-nmr and ir spectral data.
9) S. Inagaki, H. Fujimoto, and K. Fukui, J. Amer. Chem. Soc., 98, 4054 (1976).
10) J. H. Atherton and R. Fields, J. Chem. Soc. (C), 1507 (1968).
11) Though the attempted synthesis of V by the fluorination of furan tetracarboxylic acid with sulfur tetrafluoride has been reported, V was not

obtained, [B. V. Lyalin, A. V. Grigorash, L. A. Aledseeva, and L. M. Yagupol'skii, Zh. Org. Khim., 11, 460 (1975). Chem. Abstr. 83, abstract 9849 (1975).]

12) This photo-fragmentation could not be quenched by triplet quenchers (cis, trans-piperylene and isoprene).
The EPA matrix (Et_2O:iso-pentane:EtOH=1:1:1) of III was also used for the photo-reaction, but we could not obtain the isomers of V at room temperature.

13) Y. Kobayashi, I. Kumadaki, A. Ohsawa, and Y. Sekine, Tetrahedron Lett., 2841 (1974).

14) Y. Kobayashi, and A. Ando, unpublished data.
The N-substituted tetrakis(trifluoromethyl)pyrrole derivatives have also been reported, Y. Kobayashi, I. Kumadaki, A. Ohsawa, and A. Ando, J. Amer. Chem. Soc., 99, 7350 (1977).