Tetrahedron Letters No. 38, pp 3371 - 3374, 1977. Pergamon Press. Printed in Great Britain.

SYNTHESIS OF VALENCE-BOND ISOMERS OF HEXAKIS(TRIFLUOROMETHYL)OXEPIN

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

(Received in Japan 7 July 1977; received in UK for publication 1 August 1977)

We reported the photochemical conversion of hexakis(trifluoromethyl)-benzvalene ozonide (I) to tetrakis(trifluoromethyl)cyclobutadiene syn-dimer.[1] We now report the reduction of I and synthesis of the valence-bond isomers of hexakis(trifluoromethyl)oxepin.

Reduction of I with triphenylphosphine (1:1 molar ratio) at -20°C gave tetrakis(trifluoromethyl)-2,4-bis(trifluoroacetyl)bicyclo[1.1.0]butane (II) as a colorless liquid, in a quantitative yield.[2] The structure of II was determined from the following spectral data; ir (n-C_5H_{12}) 1775 cm^{-1} (C=O); mass spectrum, m/e 518 (M^+), 421 (M-$COCF_3$); ^{19}F-nmr[3] (n-C_5H_{12}) ppm, -11.2, -2.4, 13.6 (equal intensity ratio, respectively).

Compound II, which has two cis-oriented trifluoroacetyl groups was considered to have a favorable structure for reaction with trivalent phosphine to give dioxaphospholane compound or some rearranged products. Because it is known that two molar equivalents of hexafluoroacetone react with triphenylphosphine to give dioxaphospholane.[4]

Treatment of a pentane solution of II with an equivalent molar amount of triphenylphosphine in argon atmosphere at -78°C gave hexakis(trifluoromethyl)-2-oxabicyclo[3.2.0]hepta-3,6-diene (III) and hexakis(trifluoromethyl)-3-oxatricyclo[4.1.0.0^{2,7}]heptene[5] (IV), both as a volatile liquid, instead of the dioxaphospholane compound. Yield of III and IV calculated from I was 50% and 19.9%, respectively. Spectral data of III; ir (NaCl), 1700 cm^{-1} (cyclobutene double bond), 1679 cm^{-1} (enol ether double bond); mass spectrum, m/e 502 (M^+), 340 $(M$-$CF_3C{\equiv}CCF_3)^+$.

Spectral data of IV; ir (n-C_5H_{12}) 1660 cm^{-1} (enol ether double bond), 1530 cm^{-1} (cyclopropane); mass spectrum, m/e 502 (M^+), and other fragment ion peaks were very similar to that of III. ^{19}F-nmr spectral data of III and IV are shown in Chart I.

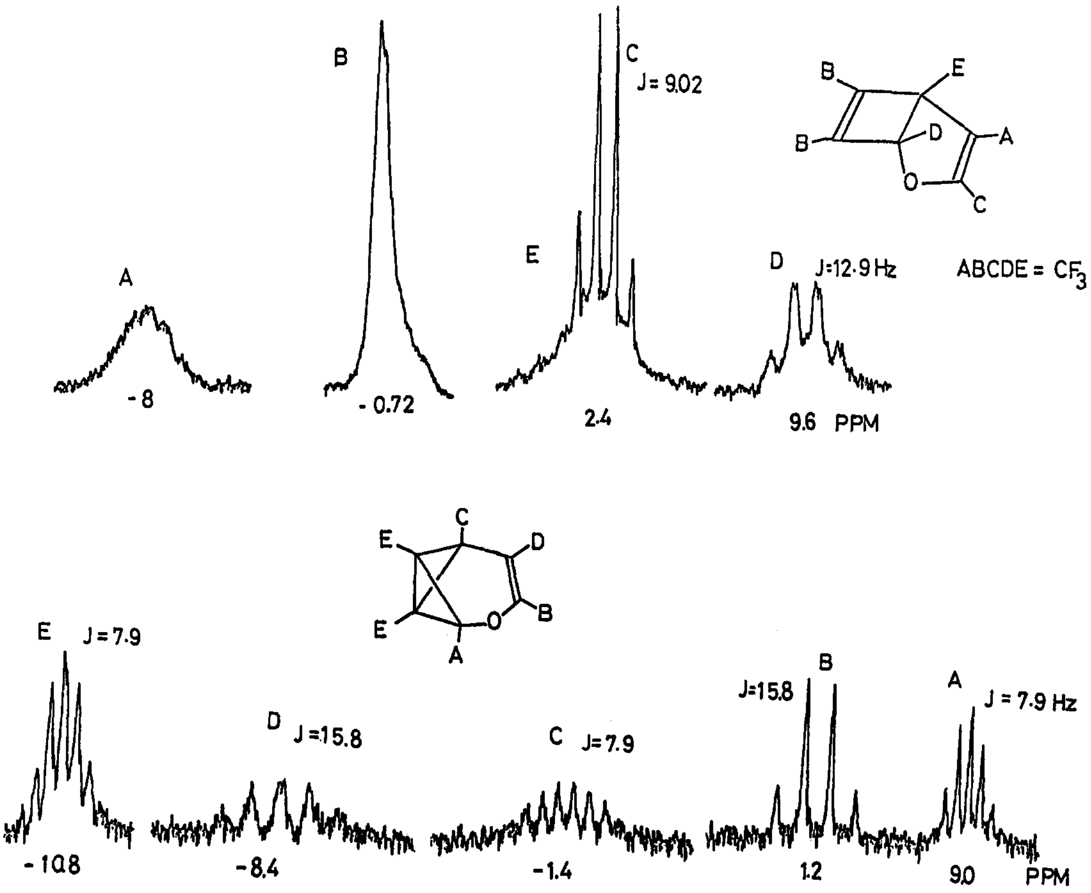

Chart I

The compound IV hereby obtained is the first example of a valence-bond isomeric system of oxepin[6] except for its benzene-fused analog.[7] The fact that the dioxaphospholane could not be obtained by the reaction of II with triphenylphosphine seems to suggest that the intermediate dioxaphospholane is thermally unstable or another intermediate is involved.

From the consideration of stereochemical models, it is impossible to construct the dioxaphospholane compound as an intermediate. Therefore, we conclude that the reasonable intermediate from II to oxepin isomers (III and IV) must be the betain compound (V). A similar intermediate has been considered from the reaction of fluorenone with trialkylphosphite.[8] This reaction scheme is shown in Fig. 1.

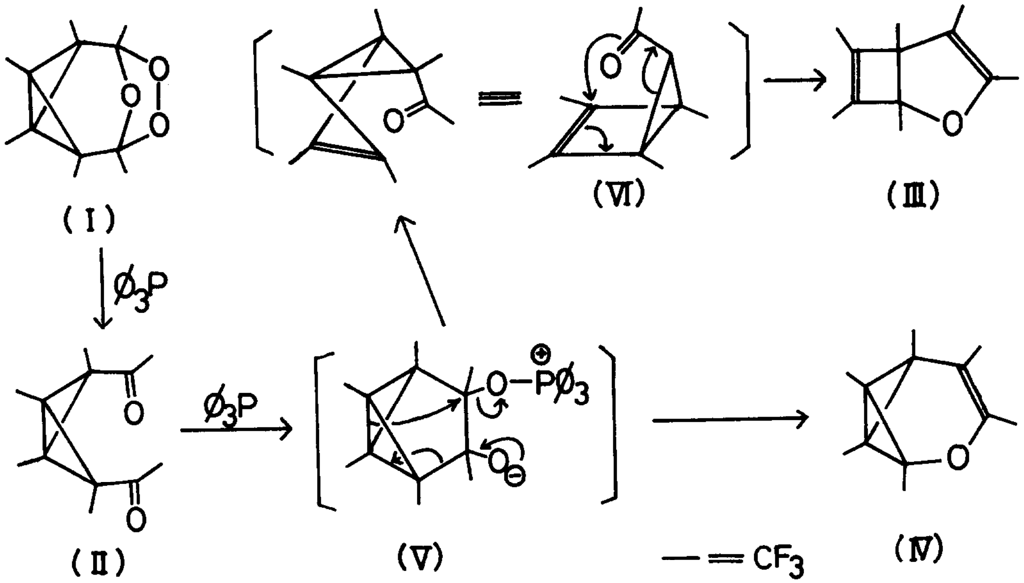

Fig. 1.

The pathway from the postulated bicyclic ketone (VI) to the product (III) has been discussed by Dreiding et al.,9) who suggested that the equilibrium of Claisen-retro-Claisen rearrangement of this system(VI⇄III) leans completely towards the enol-ether system (III). We are now investigating the reactivity of III and IV.

Refferences and Notes

1) Y. KObayashi, I. Kumadaki, A. Ohsawa, Y. Hanzawa, M. Honda, and Y. Iitaka, Tetrahedron Lett., 3001 (1975).

2) II easily forms a hydrate in the presence of moisture. Treatment of this hydrate with phosphorus pentoxide regenerates II. II was isolated using a Trap-to-Trap vacuum line. Though the reduction of nonsubstituted benzvalene ozonide was attempted by Christl using a metal hydride, compound with a bicyclobutane ring system was not obtained [M.Christl and G. Brüntrup, Chem. Ber., 107, 3908 (1974)].

3) Benzotrifluoride as an internal standard; upfield shifrs are quoted as positive.

4) F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, Tetrahedron Lett., 2151 (1966).

5) III and IV were separated by using Varian GC Model 705, 70°C, 10-m column 15% DEGS on Chromosorb W. Satesfactory high resolution mass spectra were obtained for the new compounds.

6) (i) Hydrocarbon analogous systems are known; tricyclo[4.1.0.0^{3,7}]heptene derivatives; a) C. W. Klumpp and J. J. Vrielink, Tetrahedron Lett., 539 (1972); b) M. Christl and G. Bruntrup, Angew. Chem., 86, 197 (1974); c) R. T. Taylor and L. A. Paquette, Tetrahedron Lett., 2741 (1976); d) H. Babsch, H. Fritz, and H. Prinzbach, Tetrahedron Lett., 4677 (1975); e) H. Prinzbach, H. Babsch, and H. Fritz, Tetrahedron Lett., 2129 (1976).

(ii) Review of oxepin; a) L. A. Paquette, Nonbenzinoid Aromatics, Vol. 1, in J. P. Snyder, ed, Academic Press inc., New York, 249 (1969); b) E. Vogel and H. Gunter, Angew. Chem., Int. ed, 6, 385 (1967).

7) M. Uyegaki, S. Ito, Y. Sugihara, and I. Murata, Tetrahedron Lett., 4473 (1976).

8) I. J. Borowitz, P. D. Readio, and P. Rusek, Chem., Commun., 240 (1968).

9) B. C. Baumann, M. Markert, H. Prinzbach, and A. S. Dreiding, Helv. Chem. Acta, 54, 1589 (1971).