

A NOVEL CAGE COMPOUND CONTAINING TWO PHOSPHORUS ATOMS

Yoshiro Kobayashi, Itsumaro Kumadaki, Yuji Hanzawa,

Hiroshi Hamana, and Shomi Fujino

Tokyo College of Pharmacy, Horinouchi, Hachioji-shi, Tokyo 192-03, Japan

(Received in Japan 8 October 1976; received in UK 11 November 1976)

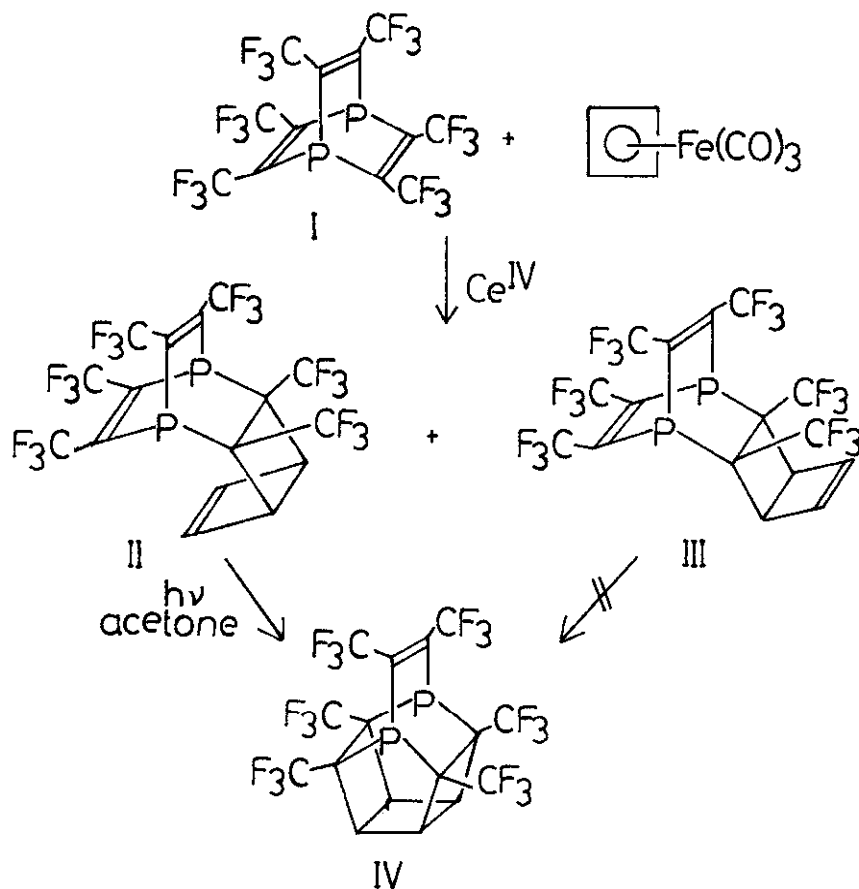
A diphospha analogue of barrelene, 2,3,5,6,7,8-hexakis(trifluoromethyl)-1,4-diphospha-bicyclo[2.2.2]octa-2,5,7-triene (I)¹⁾, had been reported to be stable to atmospheric oxygen or bromine dissolved in chloroform, because of steric hindrance of the trifluoromethyl groups. But we reported²⁾ that methanol added to a double bond of I in the presence of $RhCl_3$ and that 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphospha-benzene was derived from this adduct by thermolysis.

In this paper, we wish to report the Diels-Alder reaction of I with cyclobutadiene and a derivation to a new cage compound from the adduct.

Although compound I did not react with furan or tetraphenylcyclopentadiene, a less bulky diene was expected to react with I. Therefore, we investigated the reaction of I with cyclobutadiene. In fact, I reacted with cyclobutadiene, generated from cyclobutadiene-iron tricarbonyl, at room temperature in acetone to give two isomeric 1:1 adducts (II and III). II: 33.2%; mp 111-112° (colorless needles from chloroform); ir (KBr) 1600 cm^{-1} (C=C); 1H -nmr ($CDCl_3$) δ 3.95 (2H, b, $\geq C-H$), 6.00 (2H, b, C=C-H); ^{19}F -nmr ($CDCl_3$) δ ³⁾ -2.84 (6F, d, $J_{PF}=41.7\text{ Hz}$), -6.04 (6F, d, $J_{PF}=39.5\text{ Hz}$), -6.08 (6F, d, $J_{PF}=39.5\text{ Hz}$); mass spectrum m/e 600 (M^+). III: 23.7%; mp 97-98° (colorless needles from chloroform); ir (KBr) 1600 cm^{-1} (C=C); 1H -nmr ($CDCl_3$) δ 3.00 (2H, m, $\geq C-H$), 6.22 (2H, s, C=C-H); ^{19}F -nmr ($CDCl_3$) δ -5.40 (6F, d, $J_{PF}=40.6\text{ Hz}$); -6.06 (6F, d, $J_{PF}=38.4\text{ Hz}$), -6.16 (6F, d, $J_{PF}=33.8\text{ Hz}$); mass spectrum m/e 600 (M^+).

Next, we examined the photolysis of II and III to establish the configuration of the two isomers. Irradiation of II in acetone gave 2,5,7,10,11,12-

hexakis(trifluoromethyl)-1,6-diphosphahexacyclo[4.4.2.0^{2,5}.0^{3,9}.0^{4,8}.0^{7,10}]-dodecene-11 (IV) in 74.3% but that of III did not. This fact shows that II is an endo isomer and that III is an exo one. IV: mp 201-203°(white plates from acetone); ir (KBr) 1610 cm⁻¹ (C=C); ¹H-nmr (CD₃COCD₃) δ 3.96 (4H, s, >C-H); ¹⁹F-nmr (CD₃COCD₃) δ -1.06 (12F, d, J_{PF}=41.3 Hz), -4.80 (6F, d, J_{PF}=38.6 Hz); mass spectrum m/e 600 (M⁺). All these data support the structure of IV, which is an interesting compound of a new ring system containing two phosphorus atoms.



REFERENCES

- 1) C.G. Krespan, J. Amer. Chem. Soc., 83, 3432 (1961).
- 2) Y. Kobayashi, I. Kumadaki, A. Ohsawa, H. Hamana, Tetrahedron Lett., in press.
- 3) Benzotrifluoride: +0 ppm as an internal standard.