A Trifluoromethylated Diphosphabenzvalene: 1,3,4,6-Tetrakis(trifluoromethyl)-2,5-diphosphatricyclo[3.1.0.0^{2,6}]hexene-3

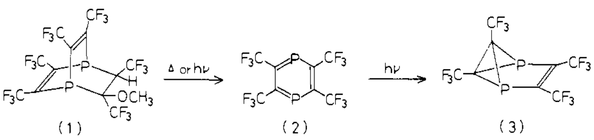
Sir:

Previously, we reported the synthesis of 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (**2**) by the thermolysis of the methanol adduct (**1**) of 2,3,5,6,7,8-hexakis(trifluoromethyl)barrelene[1] and 7,7-dichloro-2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphanorbornadiene by thermolysis of **2** with carbon tetrachloride.[2] In this work, we examined the photolysis of **2** and found that the title compound (**3**) was obtained. Compound **3** is the first example of a benzvalene analogue containing heteroatoms in the ring system. Further, photolysis of **1** was found to give **3** through **2**.

The solution of **2** in perfluoropentane, which was obtained in situ by thermolysis of **1** in *n*-hexane, evaporation of solvent, and dissolution of the residue in perfluoropentane in argon atmosphere, was sealed in a Pyrex tube under vacuum and irradiated with a high pressure mercury lamp for 72 h. Separation of the reaction mixture by a trap-to-trap distillation gave colorless oil (**3**), which solidified at −78 °C. The mass spectrum shows that **3** is a valence-bond isomer of **2**: *m/e* 386 (M^+), high mass calcd for $C_8F_{12}P_2$ 385.928, found 385.929. Presence of a double bond is confirmed by the IR spectrum ($\nu_{C=C}$ 1620 cm^{-1}). ^{19}F NMR[3] shows that **3** has two kinds of trifluoromethyl groups: δ −10.2 (d, J_{PF} = 22.6 Hz), and −6.0 (t, J_{PF} = 5.2 Hz), intensity ratio 1:1. The former couples with one phosphorus atom and the latter with two. Only one kind of phosphorus was observed in ^{31}P NMR[4]: δ 17.96 (singlet by irradiation of fluorine). These spectral data suggest that **3** is 1,3,4, 6-tetrakis (trifluoromethyl)-2, 5-diphosphatetracyclo-[3.1.0.0^{2,6}]hexene-3. The ^{13}C NMR supports this assignment (Figure 1). Compound **3** is stable against air at room temperature and thermally isomerized to **2**: half-life at 198 °C in hexafluorobenzene is ~75 min.

Compound **1** was found to give **2** at first and then **3** under the same condition as the photolysis of **2** (Scheme I). Prinzbach et al. reported[5] that the homocyclic tricyclo[2.2.2]octadiene compound was converted mainly to intramolecular [2 + 2] cycloadduct. The difference between our result and theirs might be ascribed to the longer P–C bond; two double bonds are too far to add to each other.

Scheme I



Many attempts have been made to obtain valence-bond isomers of azine and diazine compounds, but no heterocyclic analogue of benzvalene has been isolated nor observed spectroscopically. Our isolation of the diphospha analogue of benzvalene might be due to speciality of the phosphorus in the excitation, the longer P–C bond, the difference in hybridation between the first and the second row elements, and/or the perfluoroalkyl effect stabilizing strained ring systems.

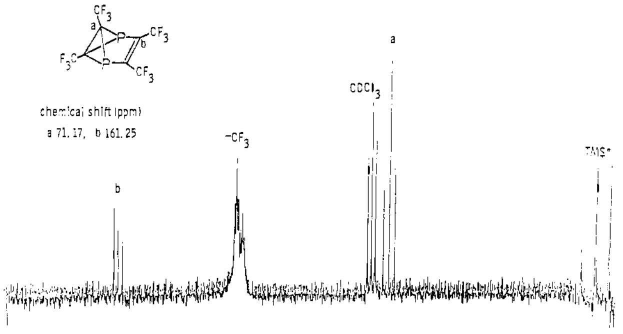


Figure 1. ^{19}F-Decoupled ^{13}C NMR: *, ^{1}H nondecoupled.

References and Notes

(1) Y. Kobayashi, I. Kumadaki, A. Ohsawa, and H. Hamana, *Tetrahedron Lett.*, 3715 (1976)

(2) Y. Kobayashi, I. Kumadaki, H. Hamana, and S. Fujino, *Tetrahedron Lett.*, 3057 (1977).

(3) Benzotrifluoride as internal standard.

(4) 85% H_3PO_4 as external standard.

(5) H. Prinzbach, W. Eberbach, H. Hagemann, and G. Philippossion, *Chem. Ber.*, **107**, 1957 (1974).

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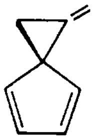
Synthesis and Properties of 1-Methylenespiro[2.4]hepta-4,6-diene. A Facile and Bond-Selective Sigmatropic Ring Expansion

Sir:

We have prepared 1-methylenespiro[2.4]hepta-4,6-diene (**1**) by the photochemical cycloaddition of diazocyclopentadiene to allene at low temperature. The material is a potential source of a substituted trimethylenemethane diradical for which considerable stabilization of the zwitterionic singlet state **4** might be expected.[1] The spirotriene **1** is unstable and undergoes a facile sigmatropic ring expansion to the bicyclic triene **2** which dimerizes in a Diels–Alder fashion to produce a highly strained and thermally labile kinetic dimer. This unprecedented low temperature ring expansion is quite possibly assisted by strain relief of the methylenecyclopropane and results in the migration of the allylic rather than the vinylic σ bond. Derivatives of bicyclo[3.2.0]hepta-1,3-diene (**5**) are extremely unstable.[2] All attempts to generate the parent system have yielded only spiro[2.4]heptadiene **6** via an unusually fast ring contraction which is apparently driven by relief of the considerable strain of the bridgehead double bond of **5**. In marked contrast, protonation of the bicyclo[3.2.0]heptatrienyl anion (**7**) apparently produces **8** as an unstable intermediate which promptly dimerizes in a [2 + 2] fashion across the strained double bond rather than undergoing the sigmatropic ring contraction.[3] It has been suggested that the latter pathway is energetically unfavorable because of the strain associated with the formation of the cyclopropene ring (E_s = 55 kcal/mol).[4] In this respect, it is interesting that the recently prepared spiro[2.4]heptatriene derivatives **9** do not ring expand under the conditions of isolation.[5] This suggests the interesting possibility that the migratory apptitude of the vinyl σ bonds may be low even though the ring expansion is conceivably exothermic.



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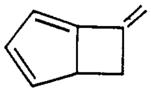

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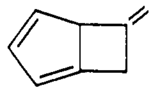

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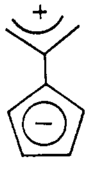

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