

THERMAL CYCLIZATION OF A 1,3-DIPHOSPHA-ALLENE. FORMATION OF A 1,2,3,4-TETRAHYDRO-1-PHOSPHANAPHTHALENE

Masaaki Yoshifuji,* Takashi Niitsu, Kozo Toyota, and Naoki Inamoto
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Tokyo 113, Japan

and

Hans H. Karsch* and Hans-Ulrich Reisacher
Anorganisch-Chemisches Institut der Technischen Universität München,
Lichtenbergstrasse 4, Garching, D-8046, F. R. G.

Abstract: Thermal reaction of 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphospha-allene resulted in novel C-C bond formation via C-H addition of an *o*-*t*-butyl group to the P=C bond to give a 1,2,3,4-tetrahydro-1-phosphanaphthalene.

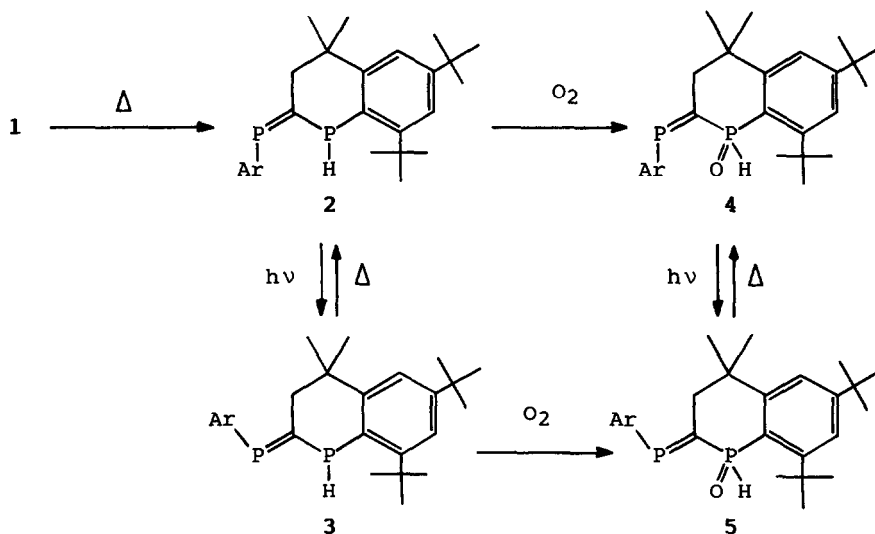
Activation and/or formation of aliphatic C-H bonds has been accomplished by transition metals¹⁾ and such reactions have been of interest in terms of mechanism and utility for organic synthesis.

In contrast, C-C activation and/or coupling reactions are much less encountered. Although several biomimetic reactions are successful in functionalizing at a selective site of substrates,²⁾ a selective C-C coupling reaction at an unactivated primary carbon atom has been difficult to achieve. We now report here an internal C-C coupling reaction to form a six-membered ring compound.

Recently, we^{3,4)} and others⁵⁾ reported the synthesis of 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphospha-allene (1), which has an interesting and novel bonding system, P=C=P. ⁶⁾



We have been interested in the character of the hetero-cumulene 1 and found that 1 reacts with some transition metals as a ligand to form complexes in η^1 and η^2 fashions,⁷⁻⁹⁾ depending on the metals employed (Cr, Mo, W, Ni, and Pt). We have found that the thermolysis of 1 involves novel intramolecular cyclization to 2-(2,4,6-tri-*t*-butylphenylphosphinidene)-6,8-di-*t*-butyl-4,4-dimethyl-1,2,3,4-tetrahydro-1-phosphanaphthalene (2) through C-H addition of an *o*-*t*-butyl group to the P=C bond resulting in C-C bond formation.⁹⁾

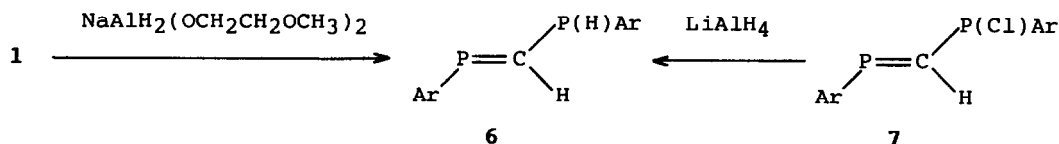


The diphospha-allene 1 (500.6 mg, 0.886 mmol) in toluene (42 ml) was refluxed for 15.5 h under argon to give a yellow solution. After evaporation of the solvent the phosphanaphthalene 2 was obtained almost quantitatively as a pale yellow powder.¹⁰ 2: mp 138 °C, ^{31}P NMR ($CDCl_3$) δ_p 251.5 (P^A, $^2J_{PP}$ = 23.2 Hz), -10.2 (P^B, $^2J_{PP}$ = 23.2 Hz, $^1J_{PH}$ = 170.9 Hz). The $^{31}P\{^1H\}$ NMR spectrum appeared as an AB pattern. 1H NMR ($CDCl_3$) 7.4-7.3 (m, 2H, arom), 7.3-7.2 (m, 2H, arom), 5.37 (dd, 1H, $^1J_{PH}$ = 170.0 Hz, $^3J_{PH}$ = 7.6 Hz, \underline{PH}), 2.3-0.5 (m, 8H, 4-Me₂+CH₂), 1.54 (s, 18H, 2xBu^t), 1.35 (s, 9H, Bu^t), 1.34 (s, 9H, Bu^t), 1.21 (s, 9H, Bu^t). $^{13}C\{^1H\}$ NMR showed a very complex spectrum at both 25 MHz and 100 MHz. Complete assignments for these peaks are in progress. MS (m/z) 508 (M⁺-CH₂=CMe₂, 11%), 231 (100%). The compound 2 was easily oxidized under atmospheric oxygen to give the corresponding 1-oxide 4. 4: ^{31}P NMR δ_p 261.1 ($^2J_{PP}$ = 36.6 Hz), 14.2 ($^2J_{PP}$ = 36.6 Hz, $^1J_{PH}$ = 506.6 Hz). Cyclization to six-membered ring is unusual and novel since the compounds carrying 2,4,6-tri-*t*-butylphenyl-phosphorus moiety usually undergo 5-membered ring formation,^{4a,11,12} and this is the first example of formation of 6-membered ring.

More interestingly, on irradiation of 2 (80 mg, 0.14 mmol) in toluene (1 ml) in an NMR tube with a medium-pressure mercury lamp at -10 °C for 30 min, the exo-cyclic phosphinidene moiety at 2-position was isomerized to E (3) to give an equilibrium mixture (2 : 3 = 1 : 1) which was identified by NMR. Prolonged irradiation did not alter the ratio. 3: ^{31}P NMR (toluene) δ_p 230.3 ($^2J_{PP}$ = 105.0 Hz), -17.7 ($^2J_{PP}$ = 105.0 Hz, $^1J_{PH}$ = 161.1 Hz). 1H NMR (C_6D_6) 6.39 (dd, $^1J_{PH}$ = 155 Hz, $^3J_{PH}$ = 8 Hz, \underline{PH}). The phosphine 3 was also oxidized to 5. 5: ^{31}P NMR (toluene) δ_p 250.7 ($^2J_{PP}$ = 107.4 Hz), 10.7 ($^2J_{PP}$ = 107.4 Hz, $^1J_{PH}$ = 473.6 Hz). On the other hand, the oxide 4 was isomerized to 5 on irradiation. Both 3 and 5 were thermally reconverted to 2 and 4 respectively, which reflects the higher steric strain of the E-isomers: At 60 °C within 12

h, the above mentioned equilibrium mixture of 2 and 3 rearranged quantitatively to pure 2. The E/Z photoisomerization around the P=C bond was observed in several phosphoethylenes.¹³⁾

The E/Z configuration around the P=C bond was determined by an empirical rule observed by Becker and Regitz.¹⁴⁾ The spin-spin coupling constants $^2J_{\text{PX}}$ between the phosphorus and the β atom X in the syn location to the lone pair of the phosphorus atom around the P=C bond is larger than that for X in the anti position.¹⁵⁾



The attempted reduction of 1 with lithium aluminum hydride did not proceed but the phosphinophosphaethylene 6 was obtained from 1 and sodium bis(methoxyethoxy)aluminum hydride. The compound 6 was purified by column chromatography. 6: ^{31}P NMR (CDCl_3) δ_{P} 280.9 ($^2J_{\text{PP}}=100.1$ Hz), -57.6 ($^2J_{\text{PP}}=100.1$ Hz, $^1J_{\text{PH}}=229.5$ Hz). The configuration of 6 appeared to be E because of the large $^2J_{\text{PP}}$ constants and was identical with that prepared by an alternative route starting from 7.^{4a)}

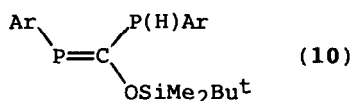


On heating under similar conditions for 1, either phosphoethylene 8 or 9 remained unchanged as it was,^{13b)} indicating that the present cyclization reaction is characteristic for the 1,3-diphospha-allene system. Studies on the mechanism for the cyclization are in process.¹⁶⁾

References and Notes

- 1) a) G. W. Parshall, Acc. Chem. Res., **8**, 113 (1975). b) M. I. Bruce, Angew. Chem., Int. Ed. Engl., **16**, 73 (1977). c) R. H. Crabtree, Chem. Rev., **85**, 245 (1985). d) H. Rabaã, J.-Y. Saillard, and R. Hoffmann, J. Am. Chem. Soc., **108**, 4327 (1986).
- 2) R. Breslow, Acc. Chem. Res., **13**, 170 (1980).
- 3) M. Yoshifuji, K. Toyota, and N. Inamoto, J. Chem. Soc., Chem. Commun., **1984**, 689.
- 4) a) H. H. Karsch, F. H. Köhler, and H.-U. Reisacher, Tetrahedron Lett., **25**, 3687 (1984). b) H. H. Karsch, H.-U. Reisacher, and G. Müller, Angew. Chem., Int. Ed. Engl., **23**, 618 (1984).
- 5) R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkhaus, and F. Knoch, ibid., **23**, 619 (1984).

- 6) M. T. Nguyen and A. F. Hagarty, J. Chem. Soc., Perkin Trans II, **1985**, 2005.
- 7) M. Yoshifuji, K. Shibayama, T. Hashida, K. Toyota, T. Niitsu, I. Matsuda, T. Sato, and N. Inamoto, J. Organometal. Chem., **311**, C63 (1986).
- 8) C. A. Akpan, M. F. Meidine, J. F. Nixon, M. Yoshifuji, K. Toyota, and N. Inamoto, J. Chem. Soc., Chem. Commun., **1985**, 946.
- 9) A part of this work was presented at the 14th Symposium on Organo-Sulfur and Phosphorus Chemistry, Urawa, Japan, January, 1986 (T. Niitsu, K. Toyota, H. Torigoe, M. Yoshifuji, and N. Inamoto: Abstract 25), at the 52nd National Meeting of the Chemical Society of Japan, Kyoto, April, 1986 (T. Niitsu, K. Toyota, M. Yoshifuji, and N. Inamoto: Abstract 1T02), and at International Conference on Phosphorus Chemistry, Bonn, September, 1986 (H. H. Karsch, A. Appelt, H.-U. Reisacher, and G. Müller: Abstract B-39).
- 10) Alternatively, the crystals of **1** were heated to 180 °C (5 min) which resulted in the formation of a yellow oil. This was shown spectroscopically to consist of pure **2** exclusively.
- 11) a) M. Yoshifuji, I. Shima, K. Ando, and N. Inamoto, Tetrahedron Lett., **24**, 933 (1983). b) J. I. G. Cadogan, A. H. Cowley, I. Gosney, M. Pakulski, and Y. Yaslak, J. Chem. Soc., Chem. Commun., **1983**, 1408. c) J. Navech, J.-P. Majoral, A. Mariem, and R. Kraemer, Phosphorus and Sulfur, **18**, 27 (1983). d) A. H. Cowley and M. Pakulski, Tetrahedron Lett., **25**, 2125 (1984). e) J. Navech, M. Ravel, and R. Kraemer, ibid., **26**, 207 (1985). f) H. H. Karsch, H.-U. Reisacher, and G. Müller, Angew. Chem., Int. Ed. Engl., **25**, 454 (1986).
- 12) The six-membered ring formation is formally similar to the thermal and photo cyclization reactions observed for 2,4,6-tri-*t*-butylthiobenzaldehyde, though not via C-C bond formation but via C-S bond formation: R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, J. Chem. Soc., Chem. Commun., **1982**, 1187.
- 13) a) M. Yoshifuji, K. Toyota, K. Shibayama, and N. Inamoto, Chem. Lett., **1983**, 1653. b) M. Yoshifuji, K. Toyota, and N. Inamoto, Tetrahedron Lett., **26**, 6443 (1985).
- 14) T. Allspach, M. Regitz, G. Becker, and W. Becker, Synthesis, **1986**, 31.
- 15) Therefore, we should correct the tentatively assigned structure for the silyloxyphosphinophosphaethylene, which is a precursor of **1**, to the E configuration (**10**),³⁾ since the ²J_{pp} observed for the phosphinophosphaethylene **10** (²J_{pp} = 26.9 Hz) was similar to that observed for **2** but not large as compared with that for **3**.



- 16) Bond energy difference between 6-membered and 5-membered ring formations is negligibly small, if we take the following values into calculation: C-H, 98; P-C, 63; P-H, 78; and C-C, 81 kcal/mol.