Photoreaction of (*E*)-1-Mesityl-2-(2,4,6-tri-*t*-butylphenyl)diphosphene

Masaaki Yoshifuji,*,† Takahiro Sato, and Naoki Inamoto
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

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Synopsis. Photoirradiation of (*E*)-1-mesityl-2-(2,4,6-tri-*t*-butylphenyl)diphosphene gave 1,2-bis(2,4,6-tri-*t*-butylphenyl)diphosphene via a cyclotetraphosphane.

In connection with our study on the photolysis of such organophosphorus compounds in low coordination states as listed below (**1**—**4**),[1,2a,3,4] an unsymmetrical diphosphene was prepared[5] and was irradiated with a mercury lamp.[6] In order to observe *E*/*Z* isomerization around the P=P double bond (**5**$\rightleftarrows$**6**) which had been observed for a symmetrical diphosphene **2** (**2**$\rightleftarrows$**7**),[2a,7] or the ligand **5** on the metal carbonyls (**1**),[1] (*E*)-1-mesityl-2-(2,4,6-tri-*t*-butylphenyl)diphosphene (**5**) was dissolved in tetrahydrofuran (THF) and was irradiated at −40 °C, monitoring by the ^{31}P NMR at −56 °C at an appropriate time interval. Figure 1 shows some selected ^{31}P NMR spectra during the photolysis through a Pyrex filter. The starting diphosphene **5**, which gives an AB quartet[5] at low field, however, afforded the symmetrical (*E*)-diphosphene **2**,[2b] on irradiation, together with the *Z*-isomer **7**,[2a,7] giving their signals at δ_P 488.3 and δ_P 367.7, respectively. The peaks due to **2** and **7** increased on long irradiation while the complicated but symmetrical signals appeared at around δ_P 0 to −50 which did not correspond to **6**. The spectrum was simulated by the parameters of AA′BB′ spin system given in Table 1 as cyclotetraphosphane (**8**), a head-to-head dimer of the starting diphosphene **5**. Figure 2 shows the simulated spectrum by LAOCOON 3.

The photolysis of 1-(pentamethylcyclopentadienyl)-

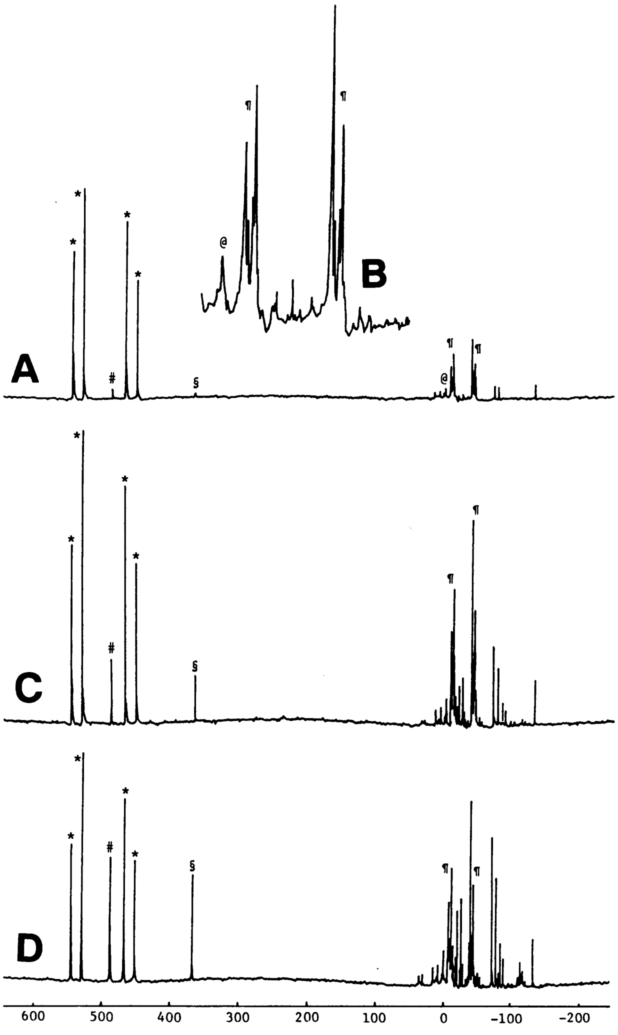
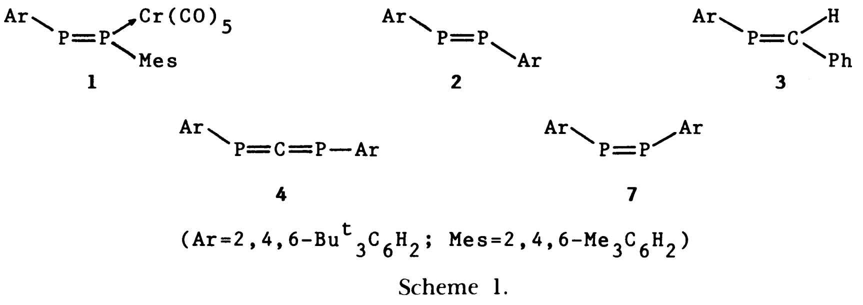


Fig. 1. ^{31}P NMR Spectra (−56 °C) during the photolysis of **5**. A) After 20-min irradiation. @: 85% H_3PO_4; *: **5**; #: **2**; §: **7**; ¶: **8** (expanded spectrum: B). C) After 52-min irradiation. D) After 121-min irradiation.

Table 1. ^{31}P NMR Parameters of **8**

Chemical shift[a]/Hz		Coupling constant/Hz	
P_1	−360	$J_{12}=J_{34}$	−160
P_2	−1529	$J_{13}=J_{24}$	25
P_3	−1529	J_{14}	−105
P_4	−360	J_{23}	−95

a) In arbitrary unit.



(Ar=2,4,6-Bu$^t{}_3$C$_6$H$_2$; Mes=2,4,6-Me$_3$C$_6$H$_2$)

Scheme 1.

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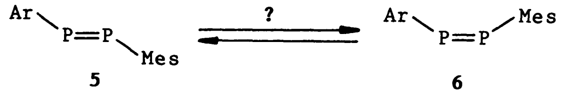
† Present address: Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980.



Scheme 2.

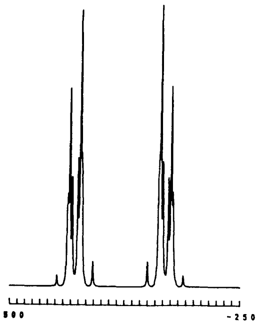
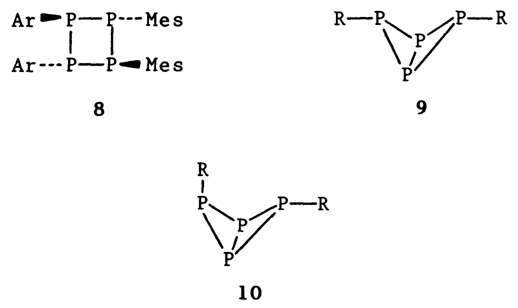


Fig. 2. Simulated spectrum of **8** with parameters listed in Table 1.



Scheme 3.

2-(2,4,6-tri-*t*-butylphenyl)diphosphene was recently reported by Jutzi and Meyer indicating the intermediacy of cyclotetraphosphanes for the formation of the symmetrical diphosphene **2** and/or bicyclo[1.1.0]tetraphosphanes like **9** or **10**.[8] Our results also suggested that an intermediate **8** decomposed to **2** followed by photo-equilibrium of **2** to **7**.

The whole process apparently resembles to a metathesis of olefins,[9] but in the present case, the other part of dimesityldiphosphene was not observed, probably because of its instability. At higher field there were observed some unknown peaks, however, it should be noted that we were not able to detect either **6**, **9**, or **10**.

In conclusion, it seems likely that photolysis of diphosphenes, depending upon the substituents and irradiation conditions, gives dimerization, cleavage, and *E*/*Z* isomerization.

Experimental

Preparation of (*E*)-1-Mesityl-2-(2,4,6-tri-*t*-butylphenyl)diphosphene (5). The diphosphene **5** was prepared according to the method described before.[5]

Photolysis of the Diphosphene 5. The diphosphene **5** (183.7 mg, 0.431 mmol) was dissolved in 1 ml of THF in an NMR sample tube of 10 mmϕ under argon and the sample was irradiated through a 2 mm thick Pyrex filter with a Riko 100-W medium-pressure mercury lamp at −40 °C. The irradiated sample was monitored by ^{31}P NMR at −56 °C at a certain time interval. Some ^{31}P NMR spectra taken at 36.3 MHz were shown in Fig. 1. The similar results were obtained after irradiation over a period of 1 h without the Pyrex filter at −75 °C. Attempts to isolate **8** failed.

Simulation of ^{31}P NMR Spectrum. The signals were analyzed as the AA′BB′ spin system by a modified version of LAOCOON 3 program. The parameters were listed in Table 1 and the simulated spectrum was shown in Fig. 2.

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