Tetrahedron Letters, Vol.32, No.47, pp 6879-6882, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

Reaction of Dichlorocarbene with Sterically Protected Phosphabutatriene. Formation of a Stable Dimethylenephosphirane

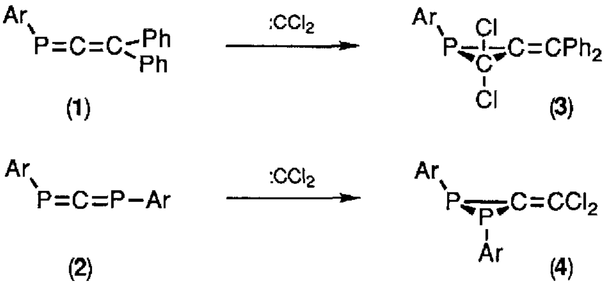
Kozo Toyota, Hideki Yoshimura, Takahiko Uesugi, and Masaaki Yoshifuji*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980, Japan

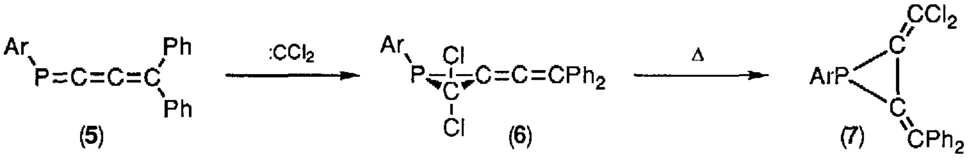
Keywords: dichlorocarbene; phosphabutatriene; phospharadialene; phosphirane; steric protection

Abstract: *The reaction of dichlorocarbene with 4,4-diphenyl-1-(2,4,6-tri-t-butylphenyl)-1-phosphabutatriene gave 2-dichloromethylene-3-diphenylmethylene-1-(2,4,6-tri-t-butylphenyl)-1-phosphirane via 2,2-dichloro-3-(2,2-diphenylethenylidene)-1-(2,4,6-tri-t-butylphenyl)-1-phosphirane.*

We have been interested in kinetic stabilization of unusual organophosphorus compounds in low coordination states. Using the 2,4,6-tri-*t*-butylphenyl moiety (hereafter abbreviated to Ar) as a protective group,[1] we have been successful in isolation and characterization of 3,3-diphenyl-1-phosphaallene (**1**)[2] and 1,3-diphosphaallene (**2**)[3] of cumulative double bonding system. We have recently reported that dichlorocarbene reacts with such phosphaallenes as (**1**) and (**2**) to give methylenephosphirane (**3**) and 3-methylene-1,2-diphosphirane (**4**), respectively.[4]

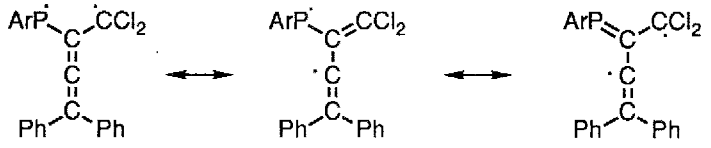


We now report the reaction of dichlorocarbene with 4,4-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phospha-1,2,3-butatriene (**5**)[5] leading to the corresponding 2,2-dichloro-3-(2,2-diphenylethenylidene)-1-phosphirane (**6**), which isomerized, on warming, to a stable phospha[3]radialene, 2-dichloromethylene-3-diphenylmethylene-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphirane (**7**).[6]

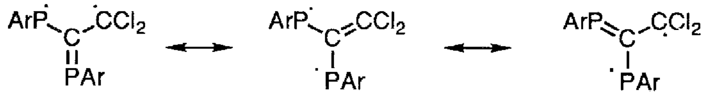


To a solution of **5** (93.3 mg, 0.20 mmol) in tetrahydrofuran (THF, 8 ml) was added 21 μl (0.22 mmol) of carbon tetrachloride at room temperature, and the mixture was cooled to –78 °C, then 0.22 mmol of butyllithium (1.44 M in hexane) was added with stirring. The solution was warmed up to room temperature and the solvent was removed in vacuo. To the residue was added 30 ml of pentane and the insoluble material was filtered off. The filtrate was concentrated and the resulting mixture was submitted to a recycling preparative high pressure liquid chromatograph LC-908 (Japan Analytical Industry, Co., Ltd., gel permeation chromatography, JAIGEL H1 + H2) to give 38.8 mg (35%) of **6**, 1.3 mg (2%) of 2,2-dichloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethylene (**8**),[7] and 2.6 mg (5%) of 1,1-dichloro-4,4-diphenyl-1,2,3-butatriene (**9**), together with 8.4 mg (9% recovery) of **5**. **6**: pale yellow crystals; mp 119 – 120 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25–7.48 (11H, m, Ph + Ar), 7.09 (1H, broad t, $^{4}J_{PH}$ = 2.0 Hz, Ar), 1.68 (9H, s, *o*-Bu^t), 1.26 (9H, s, *p*-Bu^t), and 1.20 (9H, broad s, *o'*-Bu^t); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ – 60.5; ^{13}C{^{1}H} NMR (150 MHz, THF-d_8) δ 204.1 (d, $^{2}J_{PC}$ = 9.8 Hz, C=$\underline{C}$=C), 159.8 (s, *o*-Ar), 158.6 (d, $^{2}J_{PC}$ = 9.9 Hz, *o'*-Ar), 152.6 (s, *p*-Ar), 137.3 (s, *ipso*-Ph), 131.3 (s, Ph), 130.8 (s, Ph), 130.5 (s, Ph), 130.4 (s, Ph), 130.3 (s, Ph), 130.2 (s, Ph), 129.7 (d, $^{1}J_{PC}$ = 72.1 Hz, *ipso*-Ar), 125.4 (s, *m*-Ar), 124.6 (s, *m'*-Ar), 121.3 (s, PC=C=$\underline{C}$), 100.3 (d, $^{1}J_{PC}$ = 42.5 Hz, P$\underline{C}$=C=C), 70.8 (d, $^{1}J_{PC}$ = 34.1 Hz, CCl_2) 40.6 (s, *o*-$\underline{C}Me_3$), 40.5 (s, *o'*-$\underline{C}Me_3$), 36.6 (s, *p*-$\underline{C}Me_3$), 35.8 (d, $^{4}J_{PC}$ = 10.1 Hz, *o*-C$\underline{Me_3}$), 34.9 (d, $^{4}J_{PC}$ = 5.5 Hz, *o'*-C$\underline{Me_3}$), and 32.6 (s, *p*-C$\underline{Me_3}$); UV (hexane) 235 (log ε 4.62) and 307 nm (4.27); IR (KBr) 1936, 1589, 1456, 802, 769, and 696 cm^{-1}; MS *m/z* (rel intensity) 548 (M$^+$; 22) and 513 (M$^+$–Cl; 100); Found: *m/z* 548.2168. Calcd for $C_{34}H_{39}Cl_2P$: M, 548.2167. **9**: pale yellow oil; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.2–7.5 (10H, m, Ph); MS *m/z* (rel intensity) 276 (M$^+$+4; 6), 274 (M$^+$+2; 27), 272 (M$^+$; 55), and 202 (M$^+$–2Cl; 100).

However, when the reaction of **5** with dichlorocarbene was carried out at higher temperatures, for example in refluxing hexane using the Makosza method,[8] the reaction gave the phospha[3]radialene (**7**) instead of the ethenylidenephosphirane **6**. To a mixture of **5** (70.0 mg, 0.15 mmol) and benzyltriethylammonium chloride (19 mg, 0.08 mmol), were successively added 2 ml of hexane, 2 ml of 50% aqueous NaOH soln., and 180 μl (2.24 mmol) of chloroform, and the mixture was refluxed for 2 h. The resulting mixture was poured into 30 ml of water and extracted with 10 ml of pentane for 3 times. The organic layer was washed with 10 ml of sat. NH_4Cl soln. and 10 ml of sat. NaCl soln., and dried ($MgSO_4$). After filtration, the solution was concentrated in vacuo and the flash column chromatographic separation (SiO_2 / pentane) of the residue afforded 22.7 mg (28%) of **7**, 4.3 mg (8%) of **8**, and 2.2 mg (5%) of **9**, together with 34.4 mg (49% recovery) of **5**. **7**: yellow crystals; mp 144 – 145 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34 (2H, d, $^{4}J_{PH}$ = 2.0 Hz, Ar), 6.9 – 7.3 (10H, m, Ph), 1.49 (18H, s, *o*-Bu^t), and 1.32 (9H, s, *p*-Bu^t); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ –115.7; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 156.9 (d, $^{2}J_{PC}$ = 9.4 Hz, *o*-Ar), 150.1 (s, *p*-Ar), 141.4 (s, *ipso*-Ph), 141.0 (d, $^{3}J_{PC}$ = 3.1 Hz, *ipso'*-Ph), 140.5 (d, $^{2}J_{PC}$ = 9.2 Hz, $\underline{C}Ph_2$), 133.9 (d, $^{1}J_{PC}$ = 99.1 Hz, *ipso*-Ar), 130.2 (s, Ph), 129.4 (d, J_{PC} = 3.1 Hz, Ph), 128.2 (s, Ph), 128.0 (d, $^{1}J_{PC}$ = 50.2 Hz, ArP$\underline{C}$=C), 127.9 (s, Ph), 127.8 (s, Ph), 127.4 (s, Ph), 127.4 (d, $^{1}J_{PC}$ = 44.9 Hz, ArP$\underline{C}$=C), 122.5 (d, $^{3}J_{PC}$ = 1.8 Hz, *m*-Ar), 114.2 (d, $^{2}J_{PC}$ = 17.1 Hz, $\underline{C}Cl_2$), 38.0 (s, *o*-$\underline{C}Me_3$), 34.8 (s, *p*-$\underline{C}Me_3$), 33.7 (d, $^{4}J_{PC}$ = 8.9 Hz, *o*-C$\underline{Me_3}$), and 31.3 (s, *p*-C$\underline{Me_3}$); UV (CH_2Cl_2) 241 (log ε 4.45) and 345 nm (4.25); IR (KBr) 1649, 1587, and 1550 cm^{-1}; MS *m/z* (rel intensity) 548 (M$^+$; 10) and 513 (M$^+$–Cl; 100); Found: *m/z* 548.2162. Calcd for $C_{34}H_{39}Cl_2P$: M, 548.2166. It should be noted here that the ^{13}C NMR signal assignment at δ_C = 114.2 was confirmed by a separate preparative experiment of isotope incorporation into **7** using $^{13}CHCl_3$.



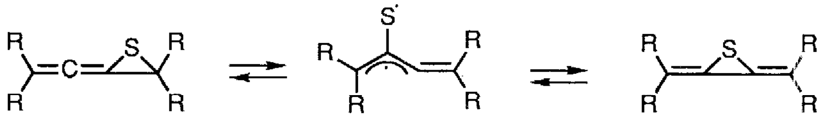
(10)



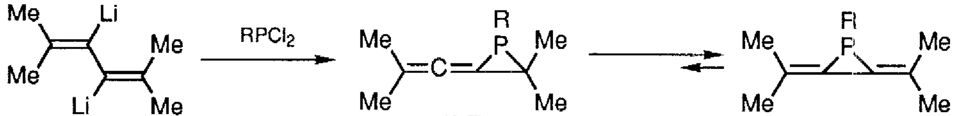
(11)

The formation of **7** at higher temperatures seems to be due to the rearrangement of initially formed **6**. In fact, the isolated **6** was refluxed in hexane for 2.5 h to give **7** almost quantitatively. This rearrangement might involve a trimethylenemethane-like intermediate (**10**) leading to a phospha[3]radialene. A similar reaction sequence has been assumed by ourselves as an intermediate **11** during the reaction of 1,3-diphosphaallene (**2**) with dichlorocarbene to give **4**,[4] although the detailed mechanism for the formation of **4** has not been clarified yet.

Isomerization from vinylidenethiirane **12** to a radialene system **13** has been reported by Ando *et al.*[9] Furthermore, Maercker and Brieden[10] have recently reported several phospha[3]radialenes **14** as reactive intermediates in the synthesis of phospha[6]radialenes. The phosphiranes **14** and **15** were prepared from the reaction of 3,4-dilithio-2,5-dimethyl-2,4-hexadiene with phosphinous dichlorides, where the thermal isomerization of **15** to **14** was observed to proceed.



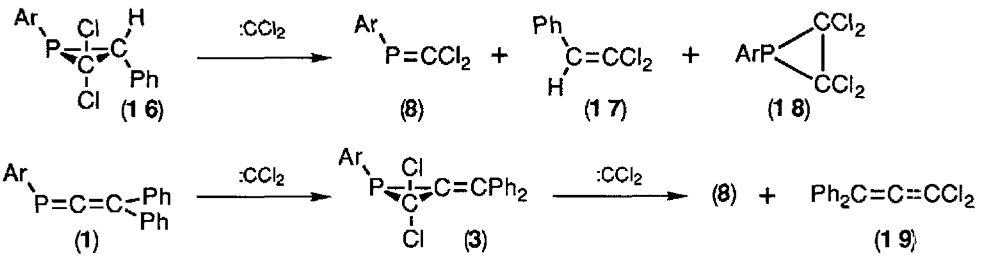
(12) (13)



(15) (14)

The formation of **8** and **9** in the carbene addition reaction is assumed to be due to the over-reaction of **6** with dichlorocarbene, taking account of the following experimental results of the reactions of excess amount of dichlorocarbene with phosphiranes: the reaction with *trans*-2,2-dichloro-3-phenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphirane (**16**)[11] gave **8** (28% yield), β,β-dichlorostyrene (**17**, 14%),[12] and 2,2,3,3-tetrachloro-1-phosphirane (**18**, 14%),[13] together with 27% recovery of the phosphirane (**16**), in contrast to the reported results on 3-chloro-3-phenyl-1,2-bis(2,4,6-tri-*t*-butylphenyl)-1,2-diphosphirane.[14]

Similarly, the phosphaallene (**1**) reacted with excess amount of dichlorocarbene to give **8** (21% yield) and 1,1-dichloro-3,3-diphenylallene (**19**, 18%), along with the initially formed methylenephosphirane (**3**, 26%) and **1** (17% recovery).



19: pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39 (10H, brs, Ph); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 200.9 ($C{=}\underline{C}{=}C$), 134.3 (*ipso*-Ph), 129.4 (*m*-Ph), 129.3 (*p*-Ph), 128.6 (*o*-Ph), and 121.4 ($Ph_2\underline{C}$); MS *m*/*z* (rel intensity) 265 (M^++5; 0.1), 263 (M^++3; 12), 261 (M^++1; 18), 260 (M^+; 0.1), and 225 (M^+–Cl; 100).

This work was supported in part by the Grants-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japanese Government (No. 03233105 and No. 02403008) and the Asahi Glass Research Fund from the Asahi Glass Foundation. The authors also thank Tosoh Akzo Co., Ltd., for donation of organolithium reagents.

REFERENCES

1. Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589; **1982**, *104*, 6167.
2. Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809–1812.
3. Yoshifuji, M.; Toyota, K.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1984**, 689–690.
4. Yoshifuji, M.; Toyota, K.; Yoshimura, H.; Hirotsu, K.; Okamoto, A. *J. Chem. Soc., Chem. Commun.*, **1991**, 124–125.
5. Märkl, G.; Sejpka, H.; Dietl, S.; Nuber, B.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1003–1004.
6. A part of this paper was presented at the 61st National Meeting of the Chemical Society of Japan, Yokohama, March 1991 (Yoshimura, H.; Toyota, K.; Yoshifuji, M.; Hirotsu, K.; Okamoto, A. *Abstract* 1C729).
7. Appel, R.; Casser, C.; Immenkeppel, M. *Tetrahedron Lett.* **1985**, *26*, 3551–3554.
8. Makosza, M; Wawrzyniewicz, M. *Tetrahedron Lett.* **1969**, 4659–4662.
9. Ando, W.; Hanyu, Y.; Kumamoto, Y.; Takata, T. *Tetrahedron* **1986**, *42*, 1989–1994; Tokitoh, N.; Hayakawa, H.; Goto, M.; Ando, W. *Chem. Lett.* **1988**, 961–964; Tokitoh, N.; Hayakawa, H.; Ando, W. *Tetrahedron Lett.* **1988**, *29*, 5161–5164.
10. Maerker, A.; Brieden, W. *Chem. Ber.* **1991**, *124*, 933–938.
11. Yoshifuji, M.; Yoshimura, H.; Toyota, K. *Chem. Lett.* **1990**, 827–830.
12. Biltz, H. *Justus Liebigs Ann. Chem.* **1897**, *296*, 263–278.
13. Yoshifuji, M.; Sasaki, S.; Inamoto, N. *Tetrahedron Lett.* **1989**, *30*, 839–842.
14. Etemad-Moghadam, G.; Tachon, C.; Gouygou, M.; Koenig, M. *Tetrahedron Lett.* **1991**, *32*, 3687–3690.

(Received in Japan 16 August 1991)