CHEMISTRY LETTERS, pp. 1053-1056, 1992.

A New Preparative Route to Phosphaethynes from Dichlorophosphaethenes by Lithiation, Photoisomerization, and Re-lithiation Involving Migration

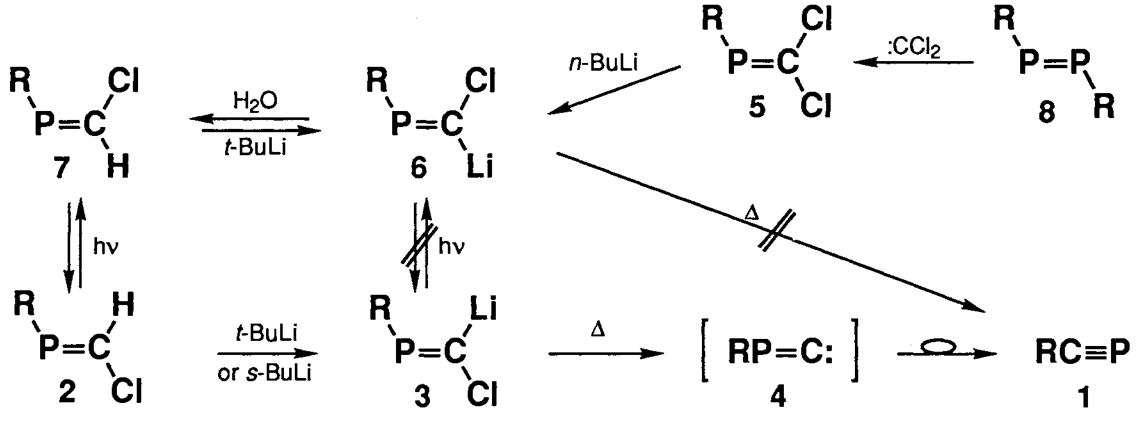
Masaaki YOSHIFUJI,* Hajime KAWANAMI, Yoshinori KAWAI, Kozo TOYOTA, Masafumi YASUNAMI,
Takashi NIITSU,† and Naoki INAMOTO†
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980
†Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

2-(2,4,6-Tri-*t*-butylphenyl)-1-phosphaethyne was prepared from 2,2-dichloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene by lithiation of *anti*-chloro atom followed by hydrolysis, photoisomerization, and repeated lithiation involving migration. The present method was successfully applied to the preparation of 2-(2,4,6-tri-*t*-pentylphenyl)-1-phosphaethyne.

Phosphaalkynes, a phosphorus analogue of nitriles, are currently of interest in view of phosphorus-containing unusual structure of coordination number 1 and of their various chemical reactivities,1) since Becker *et al.* reported a stable phosphaalkyne, 2,2-dimethyl-1-phospha-1-butyne, for the first time in 1981.2)

Recently, we have reported an interesting preparative method of 2-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethyne (**1a**) starting from (*E*)-2-chloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (**2a**) involving lithiation with *t*-butyllithium followed by migration.3) We have proposed an intermediacy of **4a**, a phosphorus analogue of isocyanide,4,5) while a very similar reaction sequence has been reported by Appel and Immenkeppel.6) The mythical compound [HP=C:] is considered to be extremely unstable compared to HC≡P according to the ab initio calculation.7)

Experimentally,8) several attempts have failed to detect **4a** so far by means of low temperature ^{31}P NMR studies. At –58 °C, when slight excess of *t*-butyllithium was added to a THF (tetrahydrofuran) solution of **2a** (14.7 mg, 0.045 mmol) in an NMR sample tube, the complete conversion of **2a** (δ_P 251.4) to the corresponding



a: R = Ar = 2,4,6-$Bu^t_3C_6H_2$; **b**: R = Aa = 2,4,6-$Pn^t_3C_6H_2$

cis-lithium compound **3a** (δ_P 330.5) was observed. On warming the mixture to –48 °C, a peak due to **1a** started to appear at δ_P 31.8,9) and the formation of **1a** was completed in 10 min at that temperature. No other peaks were observed during this ^{31}P NMR study (Fig. 1). Thus, we have not been successful in observing the formation of **4a**, even at low temperatures, which is sterically crowded and expected to be kinetically stable enough to permit isolation.10) Furthermore, attempts to trap **4a** with bis(2,4,6-tri-*t*-butylphenyl)diphosphene (**8a**)11) as a phosphinidenediphosphirane during the reaction have failed, whereas Angelici *et al.* have recently reported their successful trapping of **4a** as a platinum complex.12) In a separate experiment, the lithium reagent **3a** was quenched with methyl iodide at low temperature to give (*E*)-2-chloro-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphapropene in high yield,3) while the other (*Z*)-isomer was obtained by the methyl-iodide quenching of the corresponding *trans*-lithium compound **6a** generated either from the (*Z*)-chlorophosphaethene **7a** with *t*-butyllithium or 2,2-dichloro-1-(2,4,6-tri-*t*-butylphenyl)phosphaethene (**5a**)3) with *n*-butyllithium regardless of the quenching temperatures. It is plausible to assume that solvation about lithium atom in **3a** destabilizes its stability due to the steric congestion between the bulky 2,4,6-tri-*t*-butylphenyl group and the solvents coordinated around the lithium atom to result in the formation of **4a** or **1a**. In contrast the other *trans*-isomer **6a** is free from such steric congestion to survive in its original form even at room temperature. Moreover, it should be noted here that no formation of phosphaethyne **1a** was observed in any case from **6a**.

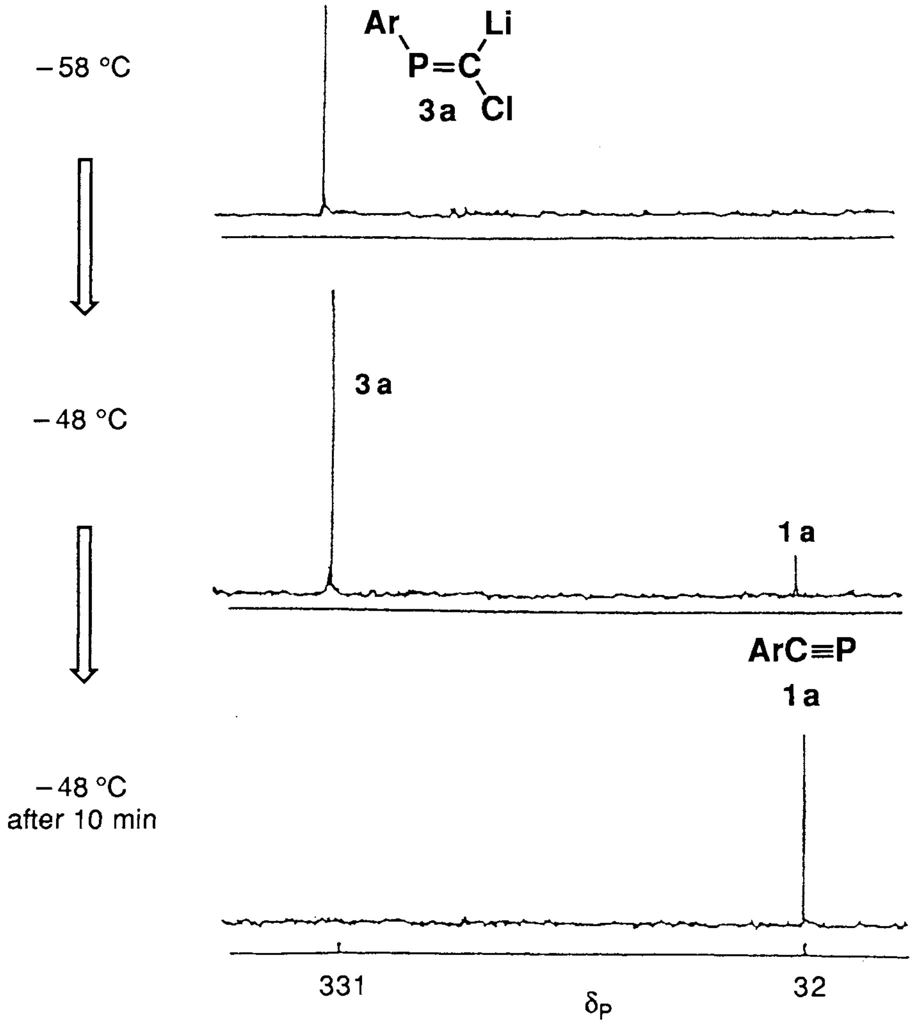


Fig. 1. Low temperature ^{31}P NMR study of the rearrangement reaction of **2a** with *t*-BuLi to **1a** *via* **3a**.

On the other hand, we have reported several photoisomerization reactions of phosphaethenes such as 2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaethenes.13) Therefore, we have attempted to apply such isomerization reactions to the preparation of the phosphaethyne **1a** as follows. Starting from dichlorophosphaethene **5a**, easily available from the corresponding diphosphene **8a**11) with large excess of dichlorocarbene,14) the lithiation was carried out at the *trans* position in THF with 1.1 equiv. of *n*-butyllithium or 2.2 equiv. of *t*-butyllithium to give **6a**, whose ^{31}P NMR peak appeared at δ_P 239.3. However, attempted irradiation of this lithio-compound **6a** with a mercury lamp at –78 °C has failed to give **3a** which was expected to isomerize to **1a**.15) When the irradiation was carried out in wet THF, an equilibrium mixture of **2a** and **7a** was obtained (36 : 64). The mixture was submitted to HPLC (Merck, LiChroprep Si 60, 8 mmϕ × 500 mm, hexane 2 ml/min) to give **2a** in 27% yield and **7a** in 48% recovery.16) Then a THF solution of **2a** was allowed to react with a slight excess of *t*-butyllithium (2.2 mol equiv.) or *s*-butyllithium (1.1 mol equiv.) to give **1a**, in 53% or 48% yield, respectively.17) **1a**: mp 125 – 127 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.31 (9H, s, *p*-Bu^t), 1.67 (18H, s, *o*-Bu^t), 7.31 (2H, d, J = 1.0 Hz, arom.); ^{13}C NMR (CDCl$_3$, 50 MHz) δ 30.81 (s, *o*-C$\underline{\text{Me}}_3$), 31.09 (s, *p*-C$\underline{\text{Me}}_3$), 35.39 (s, *p*-$\underline{\text{C}}$Me$_3$), 36.98 (*o*-$\underline{\text{C}}$Me$_3$), 121.03 (d, $^3J_{PC}$ = 1.5 Hz, *m*-arom.), 124.69 (d, $^2J_{CP}$ = 24.2 Hz, *i*-arom.), 151.25 (d, $^5J_{CP}$ = 5.9 Hz, *p*-arom.), 156.66 (d, $^3J_{CP}$ = 5.9 Hz, *o*-arom.), 168.56 (d, $^1J_{CP}$ = 55.5 Hz, C≡P); ^{31}P NMR (CDCl$_3$, 81 MHz) δ_P 33.8; IR (KBr) ν 1527 cm^{-1}; UV (hexane) λ_{max} (log ε) 231 (4.33), 237 (4.36), 244 (4.31), 306 (4.02), 319 (4.19), 335 (4.10).

Quite similarly, 2,4,6-tri-*t*-pentylphenylphosphaethyne (**1b**) was prepared as follows. Bis(2,4,6-tri-*t*-pentylphenyl)diphosphene (**8b**) was allowed to react with large excess of dichlorocarbene to give **5b** (δ_P 232.1) in 14% yield together with 3,3-dichloro-1,2-bis(2,4,6-tri-*t*-pentylphenyl)-1,2-diphosphirane (δ_P –69.0) in 34% yield.18) These compounds were purified by flash column chromatography and the compound **5b** was then allowed to react with 1.2 equiv. of butyllithium at –78 °C in THF followed by quenching with water to give **7b** in 61% yield (δ_P 248.5, d, J_{PH} = 46.7 Hz). The chlorophosphaethene **7b** was dissolved in THF and was irradiated with a mercury lamp for 1 h at –78 °C to give a mixture of **2b** and **7b** in 21 and 36% yields, respectively, after chromatographic separation. The compound **2b**19) was then allowed to react with an equivalent amount of *s*-butyllithium20) at –78 °C in THF to give **1b** in 38% yield. **1b**: mp 39.0 – 39.5 °C; δ_P (CDCl$_3$) 32.1; ^{1}H NMR (CDCl$_3$) δ 0.71 (3H, t, ^2J = 7.34 Hz, *p*-CH$_2\underline{\text{Me}}$), 0.74 (6H, t, J = 7.42 Hz, *o*-CH$_2\underline{\text{Me}}$), 1.32 (6H, s, *p*-CMe$_2$), 1.62 (12H, s, *o*-CMe$_2$), 1.66 (2H, q, J = 7.60 Hz, *p*-CH$_2$), 2.37 (4H, q, J = 7.45 Hz, *o*-CH$_2$), 7.22 (2H, s, arom.); ^{13}C NMR (CDCl$_3$) δ 168.6 (d, $^1J_{PC}$ = 54.1 Hz, C≡P). UV (hexane) λ_{max} (log ε) 232 (4.35), 237 (4.38), 246 (4.34), 308 (4.07), 320 (4.22), 336 (4.12); IR (KBr) ν 1527 cm^{-1}; Found: *m/z* 330.2476. Calcd for C$_{22}$H$_{35}$P: 330.2476. However, if *t*-butyllithium was used in place of *s*-butyllithium at the final step in the case of **2b**, $\underline{\text{no}}$ rearrangement to **1b** occurred but an alkylation took place at the *anti* 2-position of **2b** to give (*E*)-3,3-dimethyl-1-(2,4,6-tri-*t*-pentylphenyl)-1-phospha-1-butene21) in 14% yield (δ_P 238.1 (d, J = 25.0 Hz); Found: *m/z* 388.3271. Calcd for C$_{26}$H$_{45}$P: M, 388.3259), probably due to the large steric congestion against proton abstraction at the *syn* 2-position of **2b** with bulkier *t*-BuLi than *s*-BuLi.

This work was supported in part by the Grants-in-Aid for Scientific Research (No. 02403008 and 03214101) from the Ministry of Education, Science and Culture, Japanese Government and the Asahi Glass Foundation. We thank Tosoh Akzo Co., Ltd for donating organolithium reagents throughout this work.

References

1) M. Regitz, *Chem. Rev.*, **90**, 191 (1990).
2) G. Becker, G. Gresser, and W. Uhl, *Z. Naturforsch., B*, **36**, 16 (1981).

3) M. Yoshifuji, T. Niitsu, and N. Inamoto, *Chem. Lett.*, **1988**, 1733.

4) Y. Yamamoto, K. Aoki, and H. Yamazaki, *Inorg. Chem.*, **18**, 1681 (1979).

5) J. Pakusch and C. Rüchardt, *Chem. Ber.*, **122**, 1593 (1989).

6) R. Appel and M. Immenkeppel, *Z. Anorg. Allg. Chem.*, **533**, 7 (1987).

7) M. T. Nguyen and T.-K. Ha, *J. Mol. Struct.*, **139**, 145 (1986); K. K. Lehmann, S. C. Ross, and L. L. Lohn, *J. Chem. Phys.*, **82**, 4460 (1985).

8) A part of this work was presented at the 61st National Meeting of the Chemical Society of Japan. Y. Kawai, M. Yoshifuji, T. Niitsu, and N. Inamoto, Yokohama, Mar. 29 - Apr. 1, 1991, Abstr., No. 1C713.

9) G. Märkl and H. Sejpka, *Tetrahedron Lett.*, **27**, 171 (1986); *Angew. Chem., Int. Ed. Engl.*, **25**, 264 (1986).

10) S. J. Goede and F. Bickelhaupt, *Chem. Ber.*, **124**, 2677 (1991).

11) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, **103**, 4587 (1981); **104**, 6167 (1982).

12) H. Jun, V. G. Young, Jr., and R. J. Angelici, *J. Am. Chem. Soc.*, **113**, 9379 (1991).

13) M. Yoshifuji, K. Toyota, I. Matsuda, T. Niitsu, N. Inamoto, K. Hirotsu, and T. Higuchi, *Tetrahedron*, **44**, 1363 (1988).

14) M. Yoshifuji, S. Sasaki, and N. Inamoto, *Tetrahedron Lett.*, **30**, 839 (1989).

15) The quenching with methyl iodide at –78 °C after 1-h irradiation gave only Z-phosphapropene probably suggesting the absence of **3a** during the irradiation.

16) If the lithiation of a mixture of **2a** and **7a** was carried out without separating each other at –78 °C, the reaction failed to give **1a**. The reaction successfully proceeded only if *pure* **2a** was employed as a starting material, probably because more stable vinyllithium **6a** may attack **1a** even if generated as a migration product from **3a**.

17) When excess amount of *t*-BuLi was used, a further reaction occurred toward **1a** to give a *P*-alkylated product, (*E*)-3,3-dimethyl-1-(2,4,6-tri-*t*-butylphenyl)-2-phospha-1-butene (δ_P 283.5).

18) M. Yoshifuji, K. Toyota, M. Murayama, S. Sasaki, and N. Inamoto, *Science Reports Tohoku Univ., Ser. 1*, **72**, 26 (1989).

19) The compound **2b** was alternatively prepared as follows from 2,4,6-tri-*t*-pentylphenylphosphine **9b**. 2,4,6-Tri-*t*-pentylphenylphosphonous dichloride, $AaPCl_2$,^18) was reduced with $LiAlH_4$ to give **9b** (δ_P –130.4, t, J_{PH} = 130.4 Hz) almost quantitatively. The phosphine **9b** was allowed to react with chloroform and potassium hydroxide to give *E*-chlorophosphaethene **2b** in 15% yield. **2b**: mp 29.6 – 30.2 °C; δ_P 250.3 (d, J = 21.8 Hz); ^1H NMR ($CDCl_3$) δ 0.63 (6H, t, J = 7.4 Hz, $CH_2\underline{Me}$), 0.66 (3H, t, J = 7.4 Hz, $CH_2\underline{Me}$), 1.29 (6H, s, *p*-CMe_2), 1.44 (12H, s, *o*-CMe_2), 1.62 (2H, q, J = 7.4 Hz, *p*-CH_2), 6.92 (4H, dm, J = 1.91 Hz, *o*-CH_2), 7.20 (2H, d, J = 0.8 Hz, *m*-arom.), 7.29 (1H, d, J = 21.9 Hz, P=CH); ^{13}C NMR ($CDCl_3$) δ 158.73 (d, J_{PC} = 40.4 Hz, P=C); UV (hexane) λ_{max} (log ε) 243 (4.09), 211 (4.28) nm; Found: *m/z* 366.2250. Calcd for $C_{22}H_{36}P^{35}Cl$: M, 366.2244.

20) If an excess amount of *s*-BuLi was employed during the reaction, a further reaction occurred toward **1b** to give a *P*-alkylated product , (*E*)-3-methyl-1-(2,4,6-tri-*t*-pentylphenyl)-2-phospha-1-pentene (δ_P 273.2).

21) The phosphaethene was alternatively prepared from the corresponding lithium trimethylsilylphosphide and 2,2-dimethylpropanal according to a reported preparative method for ArP=C(H)Ph; M. Yoshifuji, K. Toyota, and N. Inamoto, *Tetrahedron Lett.*, **26**, 1727 (1985).

(Received March 25, 1992)