

REACTIONS OF HALOCARBENES WITH PHOSPHAALKYNE. FORMATION OF ACETYLENES *via* PHOSPHIRENE INTERMEDIATES

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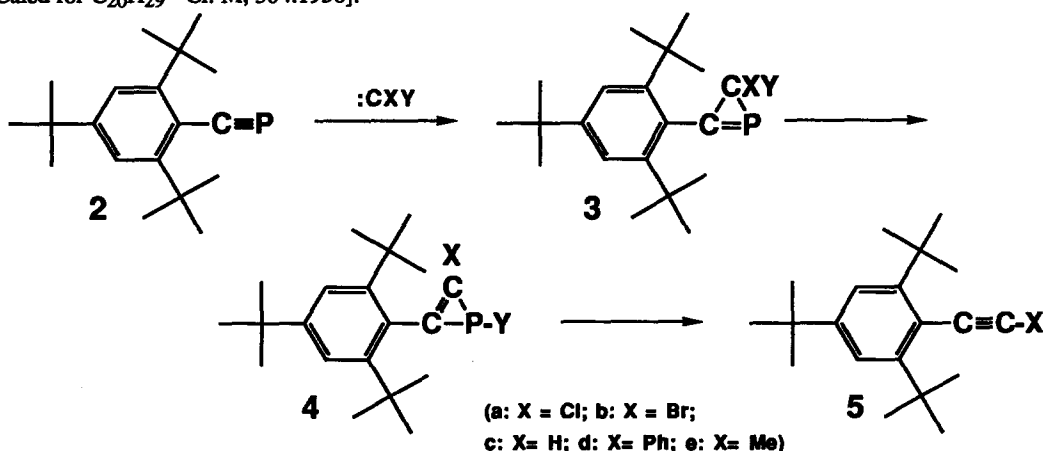
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Abstract: 2-(2,4,6-Tri-*t*-butylphenyl)-1-phosphaethyne reacted with halocarbenes to give 2,4,6-tri-*t*-butylphenylacetylenes; the reaction might proceed *via* successive 1- and 2-phosphirene intermediates followed by elimination of chlorophosphinidene.

Sterically protected phosphorus containing multiple bonded compounds have currently of interest. Among those, phosphalkynes of coordination number 1 have drawn much attention because of their various reactivities,¹ since Becker *et al.* reported the first stable phosphalkyne, 3,3-dimethyl-1-phospha-1-butyne (1).²

We have reported the 2-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethyne (2) was prepared from metallation of (*E*)-2-chloro-1-(2,4,6-tri-*t*-butylphenyl)phospha-ethylene with *t*-butyllithium through an unusual migration of the aryl group to a phosphorus analogue of isocyanide.³ We now report that the phosphalkyne (2) reacts with halocarbenes to give acetylenic compounds *via* phosphirene intermediates.

The phosphalkyne (2; 50 mg, 0.17 mmol) was dissolved in hexane (10 ml) and was allowed to react with dichlorocarbene generated from 30 equiv. of potassium *t*-butoxide and 50 equiv. of chloroform at 0 °C for 1 h. After chromatographic separation, chloro(2,4,6-tri-*t*-butylphenyl)acetylene (5a) was obtained in 45% yield [5a: mp, 105.8 - 106.2 °C; ¹H NMR (CDCl₃) δ 1.34 (s, 9H, *p*-Bu^t), 1.54 (s, 18H, *o*-Bu^t), 7.35 (s, 2H, arom.); ¹³C NMR (CDCl₃) δ 30.49 (*o*-CMe₃), 31.27 (*p*-CMe₃), 35.24 (*p*-CMe₃), 36.53 (*o*-CMe₃), 71.91 (C≡CCl), 79.31 (C≡CCl), 116.06 (*i*-arom.), 120.77 (*m*-arom.), 150.22 (*p*-arom.), 153.77 (*o*-arom.); IR (KBr) ν 2960 cm⁻¹; UV (hexane) λ_{max} (log ε) 267 (4.2), 257 (4.3), 212 (4.5) nm; Found: *m/z* 304.1958. Calcd for C₂₀H₂₉³⁵Cl: M, 304.1958].



On the other hand, dibromocarbene, generated from 50 equiv. of bromoform and 30 equiv. of potassium *t*-butoxide, reacted with the phosphalkyne 2 (47.3 mg, 0.164 mmol) at 0 °C for 1 h to give the corresponding bromoacetylene 5b, but only in 8% yield [5b: mp, 111.1 - 111.5 °C; ¹H NMR (CDCl₃) δ 1.32 (s, 9H, *p*-Bu^t), 1.53 (s, 18H, *o*-Bu^t), 7.33 (s, 2H, arom.); ¹³C NMR (CDCl₃) δ 30.48 (*o*-CMe₃), 31.28 (*p*-CMe₃), 35.27 (*p*-CMe₃), 36.51 (*o*-CMe₃), 61.33 (C≡CBr), 82.32 (C≡CBr), 116.69 (*i*-arom.), 120.73 (*m*-

arom.), 150.30 (*p*-arom.), 153.85 (*o*-arom.); IR (KBr) ν 2960 cm^{-1} ; UV (hexane) λ_{max} (log ϵ) 259 (4.2), 218 (4.4), 212 (4.5) nm; Found: m/z 348.1452. Calcd for $\text{C}_{20}\text{H}_{29}^{79}\text{Br}$: M, 338.1453].

Dichlorocarbene generated by the Makosza method in an aqueous medium⁴ reacted with the phosphalkyne **2** (48.5 mg, 0.168 mmol) at 60 °C for 6 h, however, only a trace amount of **5a** was obtained probably due to the instability of both **2** and **5** to water. Instead of **5a**, the acetylene **2c** was obtained in 3.3% yield [**5c**: mp 113–116 °C; ^1H NMR (CDCl_3) δ 1.32 (s, 9H, *p*-Bu^t), 1.58 (s, 18H, *o*-Bu^t), 3.77 (s, 1H, C \equiv CH), 7.34 (s, 2H, arom.); IR (KBr) ν 3280, 2960 cm^{-1} ; Found: m/z 270.2346. Calcd for $\text{C}_{20}\text{H}_{30}$: M, 270.2347].⁵

Chlorophenylcarbene generated from 50 equiv. of dichlorophenylmethane and 30 equiv. of potassium *t*-butoxide reacted with **1** (51.5 mg, 0.179 mmol) at 0 °C for 1 h to give phenyl(2,4,6-tri-*t*-butylphenyl)acetylene **5d** in 13% yield [**5d**: mp, 113.2–113.5 °C; ^1H NMR (CDCl_3) δ 1.36 (s, 9H, *p*-Bu^t), 1.65 (s, 18H, *o*-Bu^t), 7.36 (dddd, 1H, $J = 7.4, 7.4, 1.3, 1.3$ Hz, *p*-Ph), 7.40 (s, 2H, *m*-arom.), 7.41 (dm, 2H, $J = 7.4$ Hz, *m*-Ph), 7.55 (dm, 2H, $J = 7.0$ Hz, *o*-arom.); ^{13}C NMR (CDCl_3) δ 30.61 (*o*-CMe₃), 31.33 (*p*-CMe₃), 35.28 (*p*-CMe₃), 36.75 (*o*-CMe₃), 92.98 (C \equiv C), 101.77 (C \equiv C), 117.24 (*i*-arom.), 120.79 (*m*-arom.), 124.77 (*i*-Ph), 127.85 (*p*-Ph), 128.49 (*m*-Ph), 130.10 (*o*-Ph), 150.05 (*p*-arom.), 152.99 (*o*-arom.); IR (KBr) ν 2956 cm^{-1} ; UV (hexane) λ_{max} (log ϵ) 314 (4.6), 303 (4.4), 295 (4.6) nm; Found: m/z 346.2663. Calcd for $\text{C}_{26}\text{H}_{34}$: M, 346.2661]. However, chloromethylcarbene generated from 50 equiv. of 1,1-dichloroethane and 30 equiv. of potassium *t*-butoxide reacted with **1** (50.6 mg, 0.175 mmol) at 0 °C for 1 h to give only a trace of reaction product **5e** which is reasonable by means of the MS analysis [**5e**: m/z 284].

Regitz *et al.* reported that 3,3-dimethyl-1-phospha-1-butyne (**1**) reacts with alkylchlorocarbenes generated from the corresponding 3-alkyl-3-chlorodiazirines to give 3-alkyl-2-*t*-butyl-1-chloro-2-phosphirenes in high yield.⁶ Our reactions seem to proceed *via* 1-phosphirene (**3**) and then 2-phosphirene (**4**) followed by elimination of halophosphinidene to give the acetylene (**5**). The degradation of **4** to **5** might be attributed to the steric bulk of the aryl group. Attempts to detect polymerized chlorophosphinidene by means of ^{31}P NMR method have failed so far to confirm the reaction mechanism.

Haloacetylenes⁷ might be synthetically useful as positive halogen sources and as reagents in the coupling reactions as in the Chodkiewicz-Cadiot reaction.⁸

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