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Photolysis of (2,4,6-Tri-*t*-butylphenyl)bis(trimethylsilyl)phosphine

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Synopsis. The photolysis of (2,4,6-tri-*t*-butylphenyl)bis(trimethylsilyl)phosphine in benzene gave products suggesting homolytic P–C bond cleavage followed by rearrangement and coupling.

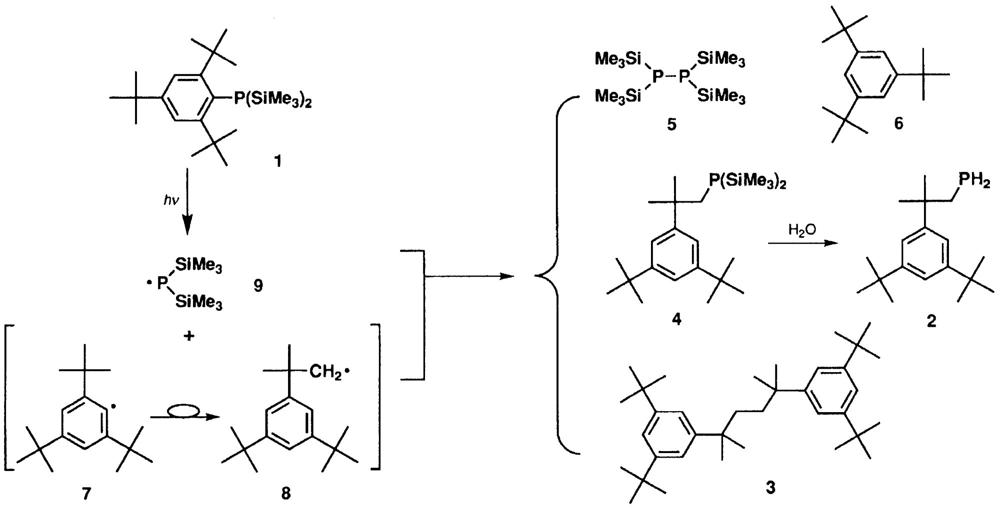
Attempts to generate a phosphinidene intermediate (RP:), as a phosphorus analog of carbenes or nitrenes, are of current interest.[1—4] We have reported the synthesis of bis(2,4,6-tri-*t*-butylphenyl)diphosphene as a kinetically stabilized diphosphene, protected by a bulky substituent, for the first time.[5] The diphosphene was considered as a dimer of the corresponding phosphinidene, although there has been no evidence for the generation of the phosphinidene intermediate during the reaction of the phosphonous dichloride with magnesium metal. On the contrary, the photolysis of this particular diphosphene with 254-nm radiation gave a 1-phosphaindan derivative as a sole product, suggesting an insertion reaction of the phosphinidene intermediate[2,4] to a C–H bond of one of the *o*-*t*-butyl groups.[3] We now report on our results of the photolysis of (2,4,6-tri-*t*-butylphenyl)bis(trimethylsilyl)phosphine (**1**)[6] to afford some products suggesting P–C bond cleavage but not P–Si bond cleavage causing a phosphinidene intermediate.[7]

Results and Discussion

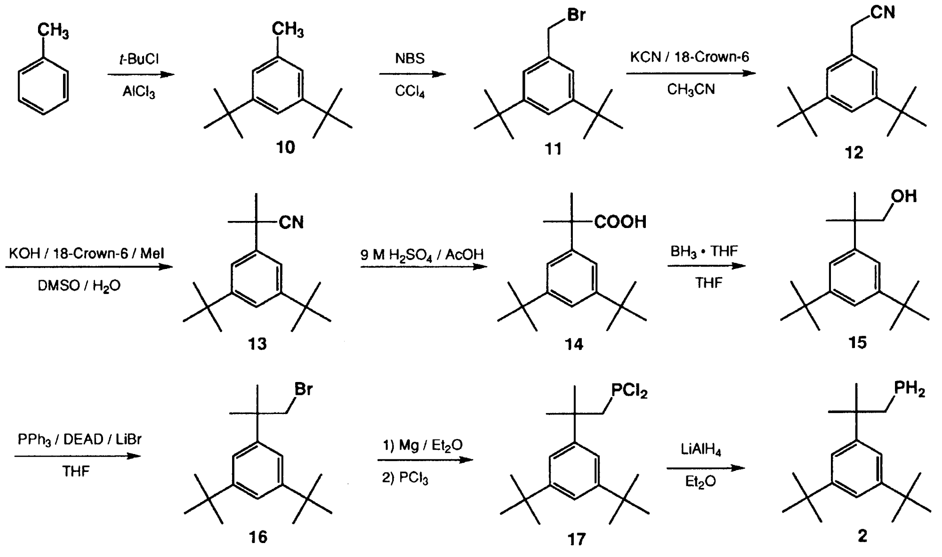
West et al.[8] reported some successful generation of silylene and its dimerization to disilene by photolysis of the corresponding disilyl derivative. Therefore (2,4,6-tri-*t*-butylphenyl)bis(trimethylsilyl)phosphine (**1**)[6] was prepared from the corresponding phosphine[9] by way of lithiation with butyllithium or *t*-butyllithium followed by silylation with chlorotrimethylsilane.[10] The disilylphosphine **1**, with a UV-vis absorption at 282 nm ($\log\varepsilon$ 3.43), was irradiated in benzene at 10 °C using a 100-W medium-pressure mercury lamp in an attempt to generate a phosphinidene intermediate. The photolysis gave some coupling products **2**—**5** and 1,3,5-tri-*t*-butylbenzene (**6**), suggesting phosphorus-carbon bond fission followed by rearrangement (Scheme 1); the bond strength for P–C and P–Si is reported to be 107.9 and 86.9 kcal mol^{-1} (1 cal=4.184 J), respectively.[11] Similar results were obtained by photolysis in a hexane solution. In the dark, however, the phosphine **1** did not decompose at all, even when heated at 80 °C for 20 h. These photolysis products indicate that the photoreaction involves P–C bond cleavage to form homolytically bis(trimethylsilyl)phosphinyl radical (**9**) and 2,4,6-tri-*t*-butylphenyl radical (**7**). Furthermore, **7** seemed to rearrange to 2-(3,5-di-*t*-butylphenyl)-2-methylpropyl radical (**8**),[7,12,13] resulting in the formation of the following products. The formation of 1,3,5-tri-*t*-butylbenzene (**6**) is probably due to H–abstraction by radical **8** or **7** from the solvent or substrate itself. The compounds tetrakis(trimethylsilyl)diphosphane (**5**)[14] and 2,5-bis(3,5-di-*t*-butylphenyl)-2,5-dimethylhexane (**3**)[12] are the known compounds and are the radical dimers of **9** and **8**, respectively. The compound, [2-(3,5-di-*t*-butylphenyl)-2-methylpropyl]bis(trimethylsilyl)phosphine (**4**), or its hydrolyzed form 2-(3,5-di-*t*-butylphenyl)-2-methylpropylphosphine (**2**), is the cross-coupling product of radicals **9** and **8**. The rearrangement products **2** and **4** thus obtained were independently prepared by authentic routes as shown in Scheme 2 to confirm the rearranged structures. Although we have not been successful in generating a phosphinidene intermediate by photolysis of **1**, we found some interesting radical coupling products that indicate homolytic cleavage of a P–C bond involving rearrangement.

Experimental

Preparation and Photolysis of (2,4,6-Tri-*t*-butylphenyl)bis(trimethylsilyl)phosphine (1). 2,4,6-Tri-*t*-butylphenylphosphine[9] (308 mg, 1.11 mmol) in tetrahydrofuran (THF, 20 mL) was lithiated with butyllithium (1.22 mmol) and silylated with chlorotrimethylsilane (1.26 mmol) at room temperature, and the process was repeated again with *t*-butyllithium (2.88 mmol) and chlorotrimethylsilane (3.00 mmol) to give **1**[6,10] in 92% yield. **1**: ^{1}H NMR (200 MHz, C_6D_6) δ=0.19 (18H, d, $^3J_{PH}$=6.1 Hz, Si$\underline{Me}_3$), 1.25 (9H, s, *p*-*t*-Bu), 1.65 (18H, s, *o*-*t*-Bu), and 7.39 (2H, d, $^4J_{PH}$=2.8 Hz, arom.); ^{13}C{^{1}H} NMR (50 MHz, C_6D_6) δ=2.84 (d, $^2J_{PC}$=17.6 Hz, Si$\underline{Me}_3$), 31.57 (s, *p*-C$\underline{Me}_3$), 34.02 (d, $^4J_{PC}$=5.6 Hz, *o*-C$\underline{Me}_3$), 34.94 (s, *p*-$\underline{C}$Me$_3$), 38.97 (d, $^3J_{PC}$=3.4 Hz, *o*-$\underline{C}$Me$_3$), 121.53 (d, $^3J_{PC}$=8.8 Hz, *m*-arom.), 127.16 (d, $^1J_{PC}$=22.9 Hz, *ipso*-arom.), 149.15 (d, $^4J_{PC}$=3.0 Hz, *p*-arom.), and 159.04 (d, $^2J_{PC}$=9.6 Hz, *o*-arom.); ^{31}P{^{1}H} NMR (81 MHz, C_6D_6, external 85% H_3PO_4) δ=−142.7; ^{29}Si{^{1}H} NMR (60 MHz, C_6D_6, internal Me_4Si) δ=5.52 (d, $^1J_{PSi}$=18.9 Hz); MS (70 eV) *m*/*z* (rel intensity) 422 (M$^+$; 27), 349 (M$^+$−Tms; 12), 275 (ArP$^+$−1; 39), 73 (Tms$^+$; 100), and 57 (*t*-Bu$^+$; 23); UV-vis (hexane) 282 nm (ε 2720). Since **1** was unstable toward moisture, the photolysis of **1** was done without further purification. The solvent was replaced with benzene (1.0 mL) and the solution was sealed in an NMR tube under argon. The solution was irradiated at 10 °C with a 100-W medium-pressure mercury lamp and was monitored by the ^{31}P NMR during the photolysis. The irradiation was stopped after 50 h when the starting silylphosphine was completely consumed. The ^{31}P NMR showed that tetrakis(trimethylsilyl)diphosphane (**5**) (δ_P=−216.3)[14] and



Scheme 1.



NBS = N-Bromosuccinimide; 18-Crown-6 = 1,4,7,10,13,16-Hexaoxacyclooctadecane; DEAD = Diethyl Azodiformate

Scheme 2.

[2-(3,5-di-*t*-butylphenyl)-2-methylpropyl]bis(trimethylsilyl)phosphine (**4**) ($\delta_P=-190.4$) were formed as major products during the photolysis. The sample tube was opened, the insoluble material was filtered off through Celite, and the filtrate was submitted to recycling HPLC (Japan Analytical Industry, Co., Ltd., LC-908) over gel permeation columns (JAIGEL H1+H2, THF as eluent) to give 2,5-bis(3,5-di-*t*-butylphenyl)-2,5-dimethylhexane[12] (**3**, 19.4 mg, 0.040 mmol, 7% yield) and 2-(3,5-di-*t*-butylphenyl)-2-methylpropylphosphine (**2**, 18.1mg, 0.065 mmol, 6% yield) together with 1,3,5-tri-*t*-butylbenzene (**6**, 82 mg, 0.333 mmol, 30% yield). The silylphosphines **4** and **5** seemed to have been hydrolyzed during the workup process. Further identification of compound **4** as well as **2** was done by the comparison of the spectral data with those of authentic samples prepared as in the following experimental part.

2: Colorless oil, ^{1}H NMR (200 MHz, $CDCl_3$) $\delta=1.36$ (18H, s, *t*-Bu), 1.42 (6H, s, $C\underline{Me_2}CH_2PH_2$), 1.97 (2H, m, $C\underline{H_2}PH_2$), 2.43 (2H, dt, $J_{PH}=195.0$ Hz, $J_{HH}=7.2$ Hz, $CH_2P\underline{H_2}$), 7.20 (2H, d, $J_{HH}=1.8$ Hz, $C_{2,6}$–H), and 7.29 (1H, t, $J_{HH}=1.8$ Hz, C_4–H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta=29.2$ (d, $J_{PC}=5.8$ Hz, $C\underline{Me_2}CH_2PH_2$), 29.2 (d, $J_{PC}=9.7$ Hz, $CMe_2\underline{C}H_2PH_2$), 31.5 ($C\underline{Me_3}$), 34.9 ($\underline{C}Me_3$), 37.9 (d, $J_{PC}=4.5$ Hz, $\underline{C}Me_2CH_2PH_2$), 119.5 ($C_4$), 119.9 ($C_{2,6}$), 147.2 ($C_1$), and 150.0 ($C_{3,5}$); ^{31}P NMR (81 MHz, $CDCl_3$) $\delta=-159.7$ (t, $J_{PH}=200.4$ Hz); MS (70 eV) m/z (rel intensity) 278 (M^+; 21) and 57 (t-Bu^+; 100); IR (neat) 2297 cm^{-1} (PH_2). Found: m/z 278.2178. Calcd for $C_{18}H_{31}P$: M, 278.2163.

3: Colorless crystals, mp 152—153 °C (ethanol, lit,[12] 150 °C); ^{1}H NMR (200 MHz, $CDCl_3$) $\delta=1.28$ (12H, s, Me), 1.35 (36H, s, *t*-Bu), 1.47 (4H, s, CH_2), 7.16 (4H, d, $J=1.7$ Hz, *o*-arom.), and 7.25 (2H, t, $J=1.7$ Hz, *p*-arom.); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta=29.2$ ($C\underline{Me_2}CH_2$), 31.6 ($C\underline{Me_3}$), 34.9 ($\underline{C}Me_3$), 37.6 ($\underline{C}Me_2CH_2$), 39.0 ($CMe_2\underline{C}H_2$), 119.0 (*p*-arom.), 119.9 (*o*-arom.), 148.7 (*ipso*-arom.), and 149.7 (*m*-arom.); MS (70 eV) m/z (rel intensity) 490 (M^+; 10), 231 (t-$Bu_2C_6H_3CMe_2^+ + 1$; 100), and 57 (t-Bu^+; 17).

When the irradiation of **1** in hexane was done in a quartz NMR tube for 20 h, the ^{31}P NMR spectrum (36 MHz) indicated that similar photolysis reaction occurred and after similar GPC column chromatographic treatment, **2** (5% yield) and **3** (4% yield) were isolated together with **6** (9% yield).

Thermal Reaction of Phosphine 1. Similarly to the above preparative experiment, the phosphine **1** was prepared starting from 2,4,6-tri-*t*-butylphenylphosphine and a benzene solution of **1** was heated in an NMR tube at 80 °C in the dark for 20 h. No change was observed in the ^{31}P NMR spectrum before and after heating.

Preparation of Authentic Samples 2—4. Starting from toluene, 2-(3,5-di-*t*-butylphenyl)-2-methylpropanenitrile (**13**)$^{15)}$ was prepared according to the methods in the literature or slightly modified methods via 1,3-di-*t*-butyl-5-methylbenzene$^{16)}$ (**10**, 54% yield from toluene), 5-bromomethyl-1,3-di-*t*-butylbenzene$^{17)}$ (**11**, 48% yield from **10**), and 5-cyanomethyl-1,3-di-*t*-butylbenzene$^{18)}$ (**12**, 90% yield from **11**), successively, in 96% yield from **12**, as shown in Scheme 2. A solution of **13** (10.2 g, 39.3 mmol) in a mixture of 9 M H_2SO_4 (50 mL) (1 M = 1 mol dm^{-3}) and acetic acid (25 mL) was refluxed for 52 h to give 2-(3,5-di-*t*-butylphenyl)-2-methylpropanoic acid (**14**, 7.29 g, 26.4 mmol, 66% yield). **14**: Colorless crystals, mp 159—160 °C (pentane); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.32 (18H, s, *t*-Bu), 1.62 (6H, s, $C\underline{Me}_2CO_2H$), 7.25 (2H, d, J=1.7 Hz, $C_{2,6}$–H), and 7.34 (1H, t, J=1.7 Hz, C_4–H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ=26.4 ($C\underline{Me}_2CO_2H$), 31.5 ($C\underline{Me}_3$), 35.0 ($\underline{C}Me_3$), 46.5 ($\underline{C}Me_2CO_2H$), 120.0 ($C_{2,6}$), 121.0 (C_4), 142.8 (C_1), 150.4 ($C_{3,5}$), and 183.3 (CO_2H); IR (KBr) 3200—2900 (OH, br) and 1699 cm^{-1} (C=O); MS (70 eV) m/z (rel intensity) 276 (M^+; 17), 261(M^+-Me; 55), 231 (M^+-CO_2H; 35), and 57 (t-Bu^+; 100). Found: C, 78.00; H, 10.34%. Calcd for $C_{18}H_{28}O_2$: C, 78.26; H, 10.14%. A solution of BH_3·THF complex (1.0 M, 30.0 mmol) in THF (30 mL) was added dropwise to a stirred solution of **14** (10.2 g, 39.3 mmol) in THF (60 mL) at 0 °C. The reaction mixture was stirred at room temperature for 15 h to give 2-(3,5-di-*t*-butylphenyl)-2-methylpropanol (**15**, 3.33 g, 12.7 mmol, 64% yield). **15**:$^{13)}$ Colorless crystals, mp 96—96.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.19 (1H, t, J=6.7 Hz, $CH_2O\underline{H}$), 1.32 (18H, s, *t*-Bu), 1.36 (6H, s, $C\underline{Me}_2CH_2OH$), 3.61 (2H, d, J=6.7 Hz, $C\underline{H}_2OH$), 7.24 (2H, d, J=1.7 Hz, $C_{2,6}$–H), and 7.31 (1H, t, J=1.7 Hz, C_4–H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ=26.4 ($C\underline{Me}_2CH_2OH$), 31.5 ($C\underline{Me}_3$), 35.0 ($\underline{C}Me_3$), 40.4 ($\underline{C}Me_2CH_2OH$), 73.3 ($CMe_2\underline{C}H_2OH$), 120.3 ($C_{2,6}$), 125.3 (C_4), 145.0 (C_1), and 150.5 ($C_{3,5}$); IR (KBr) 3400—3050 cm^{-1} (OH, br); MS (70 eV) m/z (rel intensity) 262 (M^+; 7), 247 (M^+-Me; 5), and 57 (t-Bu^+; 100). To a stirred solution of **15** (1.53 g, 5.82 mmol) and Ph_3P (4.47 g, 17.0 mmol) in THF (60 mL) was slowly added diethyl azodiformate (DEAD, 3.32 g, 19.5 mmol) at room temperature. Then LiBr (2.41 g, 27.2 mmol) in THF (40 mL) was added dropwise to that stirred solution. The reaction mixture was stirred at room temperature for 24 h to give 1-bromo-2-(3,5-di-*t*-butylphenyl)-2-methylpropane (**16**, 1.60 g, 4.92 mmol, 85% yield) after chromatographic separation (conditions: first open column chromatography eluted with hexane and then medium-pressure chromatography eluted with hexane, YMC SIL-120-50S, 20×1100 mm) to give **16**: Colorless crystals, mp 34—35 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.35 (18H, s, *t*-Bu), 1.50 (6H, s, $C\underline{Me}_2CH_2Br$), 3.60 (2H, s, CH_2Br), 7.24 (2H, d, J=1.7 Hz, $C_{2,6}$–H), and 7.33 (1H, t, J=1.7 Hz, C_4–H); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ=27.1 ($C\underline{Me}_2CH_2Br$), 31.5 ($C\underline{Me}_3$), 35.0 ($\underline{C}Me_3$), 39.3 ($\underline{C}Me_2CH_2Br$), 47.4 ($CMe_2\underline{C}H_2Br$), 120.0 ($C_{2,6}$), 120.5 (C_4), 144.9 (C_1), and 150.3 ($C_{3,5}$); IR (KBr) 1595, 1470, 1248, 893, and 714 cm^{-1}; MS (70 eV) m/z (rel intensity) 326 (M^++2; 21), 324 (M^+; 19), 203 ($M^+-Br-Me$; 100), and 57 (t-Bu^+; 27). Found: m/z 324.1433. Calcd for $C_{18}H_{29}{}^{79}Br$: M, 324.1452. A solution of **16** (308 mg, 0.948 mmol) in ether (1.0 mL) was added to magnesium metal (18.1 mg, 0.744 mg-atom) under argon at room temperature with ultrasonic irradiation (3 h). To the Grignard reagent was added PCl_3 (1.26 g, 2.06 mmol) at −78 °C and the mixture was gradually warmed up to room temperature to give 2-(3,5-di-*t*-butylphenyl)-2-methylpropylphosphonous dichloride (**17**, δ_P=194.2). The dichloride **17** in ether (5 mL), without purification, was added to $LiAlH_4$ (19.9 mg, 0.524 mmol) in ether (2 mL) at 0 °C, and was refluxed for 30 min. Insoluble material was filtered off and the filtrate was concentrated and submitted to recycling HPLC over gel permeation columns (JAIGEL H1+H2, THF as eluent) to give 2-(3,5-di-*t*-butylphenyl)-2-methylpropylphosphine (**2**, 20.5 mg, 0.0736 mmol, 8% yield) together with 2,5-bis(3,5-di-*t*-butylphenyl)-2,5-dimethylhexane (**3**, 91.3 mg, 0.186 mmol, 20% yield) and 1,3,5-tri-*t*-butylbenzene (**6**, 8.70 mg, 0.0353 mmol, 4% yield) as by-products. The spectral data of the phosphine **2** were identical with those obtained from the photolysis of **1**. Furthermore, the phosphine **2** was converted to the corresponding bis(trimethylsilyl)phosphine (**4**), as follows. The phosphine **2** (19.7 mg, 0.071 mmol) in THF (2 mL) was allowed to react with butyllithium (0.082 mmol) and then chlorotrimethylsilane (0.087 mmol) and repeatedly allowed to react with *t*-butyllithium (0.096 mmol) and then chlorotrimethylsilane (0.1 mmol) to give **4** (δ_P=−190.4), which was easily hydrolyzed to **2**. The chemical shift as well as chemical behavior of the compound **4** was identical with that obtained from the photolysis of **1**.

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