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PHOTOISOMERIZATION OF BENZYLIDENEPHOSPHINE CONTAINING PHOSPHORUS IN LOW COORDINATION STATE

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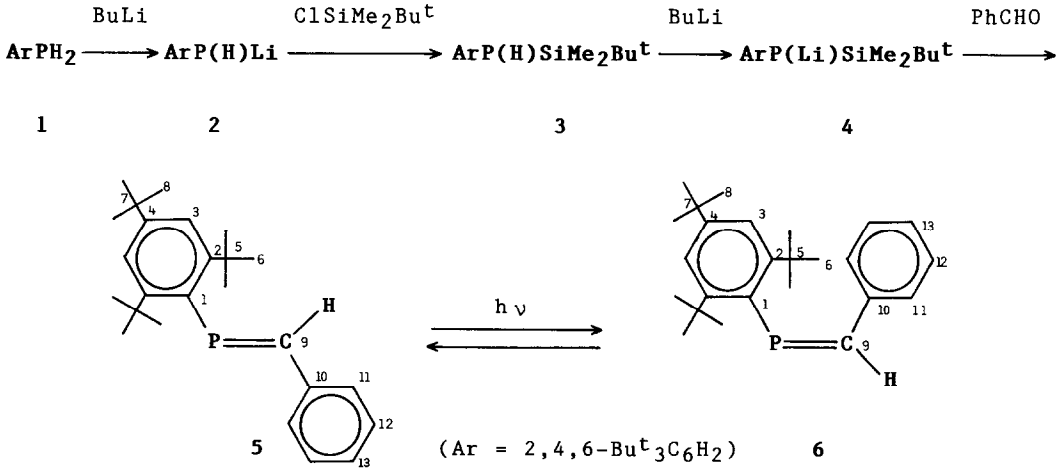
E-Benzylidene-P-2,4,6-tri-t-butylphenylphosphine containing phosphorus in low coordination state was irradiated to give the corresponding Z-isomer: both isomers were isolated and characterized and the reactions with chromium(0) carbonyls were described.

The pioneering work by Bickelhaupt et al. on the isolation of P-mesityldiphenylmethylenephosphine, $2,4,6\text{-}Me_3C_6H_2P{=}CPh_2$,[1] has stimulated the strong interest among organic and inorganic chemists to study such compounds as those with multiple bond(s) containing phosphorus or higher elements in lower coordination state.[2]

We have been interested in the isolation and characterization of the sterically protected unusual organophosphorus compounds involving -P=P-,[3] -P=C<,[4] -P=C=N-,[5] -P=C=C<,[5] -P=C=P-,[6] -P=N-,[7] and so on.[8]

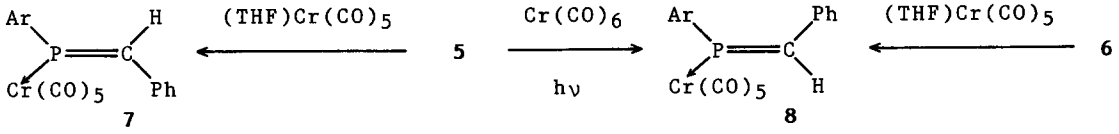
We now wish to report our preliminary results on photoisomerization of E-benzylidene-P-2,4,6-tri-t-butylphenylphosphine (**5**) to the corresponding Z-isomer (**6**). The reaction sequence employed here was as follows. t-Butyldimethylsilyl-(2,4,6-tri-t-butylphenyl)phosphide (**4**) was prepared in 35 mL of THF from the



corresponding phenylphosphine (**1**, 465 mg, 1.67 mmol) followed by lithiation with butyllithium (**2**), silylation with t-butyldimethylsilyl chloride (**3**), and repeated lithiation with butyllithium and **4** was allowed to react with benzaldehyde (2.36 mmol) to give **5**. The resulting products was purified by silica-gel column chromatography (80% yield). When the E-isomer (**5**) was irradiated with a 100-W medium pressure mercury lamp for 6 h at 0°C, the isomerization reaction was observed to give an equilibrium mixture of E and Z isomers (**5** : **6** = 3 : 7 estimated from ^{31}P NMR), and the mixture was separated by means of silica-gel column chromatography to give **5** and **6** in 32 and 66% yields, respectively.

Furthermore, when the Z-isomer (**6**) thus isolated was irradiated with a mercury lamp in benzene for 2 h at 0°C, a mixture of **5** and **6** was obtained (2 : 3). On the other hand, even if **5** was heated in toluene at 100°C for 24 hr, no isomerization reaction was observed. The phenyl and vinylic protons of **6** appeared at higher fields than those of **5**. The observed shift is characteristic for Z isomers.[4] Table 1 shows some physical constants and spectral data of the isomers thus obtained. This is the first example of the isolation of a stable Z-methylenephosphine without any heteroatom substituents.[4,9]

When the E-isomer (**5**, 20.5 mg, 0.056 mmol) was allowed to react with $(THF)Cr(CO)_5$ (0.068 mmol) in 5 mL of THF at room temperature,[10] the corresponding P-coordinated chromium complex (**7**) was obtained in 71% yield after the chromatographic treatment. Very similarly **6** was allowed to react with $(THF)Cr(CO)_5$ to give **8**. When **5** (130.2 mg, 0.356 mmol) was irradiated in the presence of excess of hexacarbonylchromium(0) (111.7 mg, 0.508 mmol) with the mercury lamp in 10 mL of THF at 0°C the Z-phosphine complex (**8**) was obtained in 54% yield. Table 2 shows some physical constants and spectral data of the complexes **7** and **8**.[11]



7 **8**

It should be noted here that a similar reaction of the silylphosphide (**4**, starting from 0.44 mmol of **1** in 10 mL of THF) with benzophenone (116.1 mg, 0.64 mmol) in 5 mL of THF at -78°C failed to give the corresponding diphenylmethylenephosphine, although the reaction mixture turned dark green immediately after mixing together and strong ESR signals were observed during the reaction. The signal assignments have been unsuccessful so far except for providing the information that an electron transfer is involved during the reaction.

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Table 1. Some Physical Constants and Spectral Data of **5** and **6**

Compound		**5**	**6**
Mp/ °C		152 - 153	95 - 97
^{31}P NMR ($CDCl_3$)/ δP ($^2J_{PH}$/Hz)		259.3 (d, 26.9)	241.6 (d, 39.1)
^1H NMR ($CDCl_3$)/ δ (J_{PH})	=CH	8.12 (d, 25.3)	7.80 (d, 37.8)
	Ar	7.44 (d, 1.3)	7.47 (d, 1.1)
	Ph	7.6 - 7.2 (m)	7.0 - 6.1 (m)
	o-Bu^t	1.52	1.47
	p-Bu^t	1.36	1.40
$^{13}C\{^1H\}$ NMR ($CDCl_3$)/ δ (J_{PC}/Hz)	C(1)	139.0 (d, 53.1)	136.4 (d, 62.9)
	C(2)	154.1 (s)	153.8 (d, 1.2)
	C(3)	121.7 (s)	122.4 (s)
	C(4)	149.7 (s)	150.9 (s)
	C(5)	38.3 (s)	38.1 (s)
	C(6)	33.9 (d, 7.3)	32.6 (d, 7.9)
	C(7)	35.0 (s)	35.1 (s)
	C(8)	31.4 (s)	31.5 (s)
	C(9)	175.8 (d, 34.8)	162.7 (d, 48.8)
	C(10)	140.2 (d, 13.7)	138.8 (d, 23.8)
	C(11)	128.6 (d, 2.8)	127.3 (d, 6.1)
	C(12)	125.8 (d, 22.0)	129.3 (d, 12.8)
	C(13)	127.8 (d, 7.3)	127.9 (d, 3.7)
UV (hexane) / λ_{max} (ε)		211 (26800)	211 (24700sh)
		238 (16900)	238 (13300)
		315 (17100)	305 (20800)
			343 (2700sh)
MS (M^+) / Found m/z		366.2443	366
(Calcd)		(366.2474)	(366)

Table 2. Some Physical Constants and Spectral Data of **7** and **8**

Compound		**7**	**8**
Mp/ °C		108 - 109	105 (decompn)
^{31}P NMR ($CDCl_3$)/ δP ($^2J_{PH}$/Hz)		263.3 (d, 29.3)	237.1 (d, 14.7)
^1H NMR ($CDCl_3$)/ δ (J_{PH})	=CH	8.61 (d, 27.5)	7.82 (d, 16.5)
	Ar	7.7 - 7.1 (m)	7.54 (d, 2.6)
	Ph		7.1 - 6.1 (m)
	o-Bu^t	1.66	1.57
	p-Bu^t	1.34	1.39
IR (KBr) ν/cm^{-1}		2070, 1990, 1960	2070, 1984
		1946, 1930	1940, 1928
MS (M^+) / Found m/z		558	558

spectra. We thank Shin-Etsu Chemical Company, Ltd., for donation of silyl chlorides used in this work.

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11) The isomer **5** reacted with excess elemental sulfur in benzene in the presence of diazabicyclo[5.4.0]undec-7-ene to give **10** (and **10'**), while monitoring the reaction by ^{31}P NMR an intermediacy of **9**, δ_P(PhH)=152.1, was

observed. **10** (Major): Mp 164-165 °C (79% yield); $\delta_P(CDCl_3)$=-7.0; ^1H NMR ($CDCl_3$) δ=7.7-7.2 (m, 7H, arom.), 3.84 (d, J=3.3 Hz, 1H, CH), 1.76 (s, 9H, o-Bu^t), 1.59 (s, 9H, o'-Bu^t), and 1.32 (s, 9H, p-Bu^t). Found: m/z 430.1899. Calcd for $C_{25}H_{35}PS_2$: M, 430.1916. **10'** (Minor): Oil (14% yield); $\delta_P(CDCl_3)$=-7.5; ^1H NMR ($CDCl_3$) δ=7.1-6.2 (m, 7H, arom.), 4.21 (d, J=5.3 Hz, 1H, CH), 1.76 (s, 9H, o-Bu^t), 1.33 (s, 9H, o'-Bu^t), and 1.31 (s, 9H, p-Bu^t). The predominant isomer might be assignable to the trans configuration about the two aryl groups taking the steric repulsion into account.

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