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REACTION OF A DIPHOSPHENE WITH BUTYLLITHIUM

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1,2-Bis(2,4,6-tri-t-butylphenyl)diphosphene reacted with butyllithium to give 1-alkyl-2-butyl-1,2-bis(2,4,6-tri-t-butylphenyl)diphosphanes after quenching with various alkyl halides, sulfurization of which afforded diphosphane monosulfides.

Diphosphenes[1-8] have been of current interest since we reported the synthesis and characterization of E-1,2-bis(2,4,6-tri-t-butylphenyl)diphosphene (1)[1] as the first isolated stable compound with a P=P bond.

We recently reported the reaction of 1 with chlorine,[1] m-chloroperbenzoic acid,[9] sulfur,[10] aluminum hydrides,[11] and hexacarbonylchromium(0).[12] We now report the reaction of 1 with butyllithium to give lithium phosphinophosphide (2) which afforded diphosphanes (3) after quenching with various alkyl halides.

$$\underset{1}{ArP=PAr} + BuLi \longrightarrow \underset{2}{[ArP^{-}-PAr(Bu)]Li^{+}} \xrightarrow{RX} \underset{3}{Ar(R)P-PAr(Bu)} \xrightarrow{S_8}$$

$$\underset{4}{Ar(R)P-P(S)Ar(Bu)} \xrightarrow{HCl} \underset{5}{Ar(R)PH} + \underset{6}{[Ar(Bu)P(S)Cl]}$$

(Ar = 2,4,6-$Bu^t_3C_6H_2$; R = Me, Et, Pr, Bu, Oct, $PhCH_2$, $PhCH_2CH_2$, t-$BuCH_2$)

A typical procedure for these reactions was as follows: to the diphosphene 1 in tetrahydrofuran (THF) was added butyllithium (1.5 equiv.) at 20 °C under argon to give a wine red homogeneous solution. The ^{31}P NMR spectrum of 2 appeared as an AB quartet;[13] the phosphide phosphorus resonated at higher field (-86.0 ppm from external 85% H_3PO_4) than that of phosphino phosphorus (-9.1 ppm), where the spin-spin

coupling constant between them was large ($^1J_{PP}$ = 344.2 Hz). The quenching of the phosphide (2) with butyl bromide gave 1,2-dibutyl-1,2-bis(2,4,6-tri-t-butylphenyl)-diphosphane (3d; R = Bu). The diphosphane, however, was not stable enough to permit isolation in the pure state by means of column chromatography. After adding elemental sulfur (1.5 equiv.) to 3d, a monosulfide was obtained and the sulfide 4d was purified through chromatography over silica gel. 4d: high resolution mass spectrum, Found: m/e 698.5115. Calcd for $C_{44}H_{76}P_2S$: M, 698.5141; ^{1}H NMR ($CDCl_3$) δ 7.37 (br s, 4H, arom.), 2.50 (m, 2H, $PrCH_2P^b$), 1.65 and 1.44 (s + s, 18H + 18H, o-Bu^t), 1.29 (s, 18H, p-Bu^t), 1.91 - 0.60 (m, 16H, Bu and $PrCH_2P^b$); IR (KBr) $\nu_{P=S}$ 600 cm^{-1}. The structures of the sulfides 4 were also chemically confirmed by the cleavage of the P-P bond with hydrogen chloride in benzene giving 5. The phosphines 5a - h were identified by the comparison with authentic samples (5a - d, g, h), prepared from the corresponding lithium phosphide[14] and alkyl halides, and/or determined by MS (5a, d - f).

Table 1 shows the ^{31}P NMR data of the phosphorus compounds (3 - 5) thus obtained. The diphosphanes 3 showed complicated spectra in some cases, however, monosulfides 4 gave a simple AB quartet pattern. The further sulfurization in the presence of excess sulfur failed to give diphosphane disulfides,[15] probably because of the large steric hindrance in the molecules 4.

According to the ^{31}P NMR analysis of the compounds 3 and 4, the products obtained seemed to be the dl isomers, since the meso isomers might suffer from the strong steric congestion in case the gauche effects are operative.[11]

The coupling constants $^1J_{PP}$ observed in 4 are fairly large probably because of a contribution from the structure of $>P^+ = \overset{v}{P}\text{-}S^-$.[16] This structure might also explain unusual low field shifts of α-protons to P^b(III) in 4 in their ^{1}H NMR spectra. These protons appeared complicatedly, but some of them (4a and 4f) could be analyzed by the multiple spin systems and tetatively assigned as follows. 4a: $^2J_{HP^b}$ = 5.4 Hz, $^3J_{HPP^a}$ = 21.9 Hz, and $^1J_{PP}$ = 310.1 Hz. 4f: $^2J_{HP^b}$ = 4.9 Hz, $^3J_{HPP^a}$ = 22.8 Hz, and $^1J_{PP}$ = 329.1 Hz. The α-methylene protons of the butyl group to P^a(V) seemed very complicated and appeared in the normal aliphatic region. It should be noted that $^2J_{HP}$ is smaller than $^3J_{HPP}$ in each case.[17]

Attempts to isolate 6 have been unsuccessful so far. In contrast to a similar phosphinothioic chloride[18] 6 seemed very unstable resulting inorganic polymeric species which appeared at δ_P (C_6H_6) 101.7 ppm in every cleavage reaction of 4a - h with excess hydrogen chloride and was assumed to be $(Cl\text{-}P{=}S)_n$, the peak height of which was almost equal to that of 5 on immediate measurement of each reaction mixture.

Table 1. ^{31}P NMR Data of the Compounds (3 - 5)

Compd	RX	Ar(Bu)P—P(R)Ar (3)	Ar(Bu)P(=S)a—Pb(R)Ar (4)			Ar(R)P-H (5)
		δ_P(THF)/ppm[a] (J_{PP}/Hz)	δ_P($CDCl_3$)/ppm (J_{PP}/Hz) a b	Yield %[d]	Mp °C	δ_P(C_6H_6)/ppm (J_{PH}/Hz)
a	MeI	[b]	56.1 -50.1 (310.1)	38	[e]	-91.4 (222.2)
b	EtI	-19.5 -23.6 (170.3)	55.5 -31.4 (322.3)	36	[e]	-68.3 (219.7)
c	PrBr	-24.1[c]	56.1 -37.4 (319.8)	28	63.5-65.5	-74.1 (219.7)
d	BuBr	-23.1[c]	56.2 -36.6 (319.8)	42	61 - 64.5	-73.4 (219.7)
e	$C_8H_{17}Br$	-23.2[c]	56.2 -36.6 (321.0)	35	[e]	-73.2 (217.3)
f	$PhCH_2Cl$	-22.9[c]	57.0 -28.5 (329.1)	48	95 - 97	-63.4 (219.7)
g	$PhCH_2CH_2Br$	[b]	56.3 -37.1 (317.4)	28	91.5-94	-73.6 (219.7)
h	t-$BuCH_2I$	-18.7 -34.8 (222.2)	62.4 -37.5 (334.5)	36	83 - 89	-86.0 (217.3)

a) Chemical shift from ext. 85% H_3PO_4. b) Complicated, however, in the following cases, a part of AB pattern was observed and tentatively assignable to diphosphanes. 3a: -24.0 and -24.6 ppm; 3g: -23.6 and -23.8 ppm. c) The spectrum appeared as a singlet probably by chance. d) Isolated yield from the diphosphene 1. e) Oil.

The formation of the phosphinophosphide 2 was also observed according to the ^{31}P NMR analysis on addition of butyllithium in excess either in ether or in THF to 1,2-bis(2,4,6-tri-t-butylphenyl)diphosphene 1-sulfide (7),[10] probably due to the facile desulfurization from the diphosphene monosulfide 7.

The reason why 4 were selectively obtained has been unclear so far, especially in the cases of 4a - c, because only taking the steric hindrance into account, the other isomers seem more favorable. Further mechanistic studies on these reactions are in progress.

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References

1) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Am. Chem. Soc., 103, 4587 (1981); 104, 6167 (1982); M. Yoshifuji, K. Shibayama, N. Inamoto, T. Matsushita, and K. Nishimoto, ibid., 105, 2495 (1983).
2) G. Bertrand, C. Couret, J. Escudié, S. Majid, and J.-P. Majoral, Tetrahedron Lett., 23, 3567 (1982); C. Couret, J. Escudié, and J. Satgé, ibid., 23, 4941 (1982); J. Escudié, C. Couret, J. D. Andriamizaka, and J. Satgé, J. Organomet. Chem., 228, C76 (1982).
3) B. Çetinkaya, A. Hudson, M. F. Lappert, and H. Goldwhite, J. Chem. Soc., Chem. Commun., 1982, 609; B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, and H. Goldwhite, ibid., 1982, 691.
4) A. H. Cowley, J. E. Kilduff, T. H. Newman, and M. Pakulski, J. Am. Chem. Soc., 104, 5820 (1982); A. H. Cowley, J. E. Kilduff, M. Pakulski, and C. A. Stewart, ibid., 105, 1655 (1983); A. H. Cowley, J. E. Kilduff, S. K. Mehrotra, N. C. Norman, and M. Pakulski, J. Chem. Soc., Chem. Commun., 1983, 528.
5) C. N. Smit, Th. A. van der Knaap, and F. Bickelhaupt, Tetrahedron Lett., 24, 2031 (1983).
6) H. Vahrenkamp and D. Wolters, Angew. Chem., Int. Ed. Engl., 22, 154 (1983).
7) K. M. Flynn, M. M. Olmstead, and P. P. Power, J. Am. Chem. Soc., 105, 2085 (1983).
8) E. Niecke, R. Rüger, M. Lysek, S. Pohl, and W. Schoeller, Angew. Chem., Int. Ed. Engl., 22, 486 (1983).
9) M. Yoshifuji, I. Shima, K. Ando, K. Toyota, and N. Inamoto, J. Chem. Soc., Chem. Commun., 1983, 419.
10) M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Chem. Soc., Chem. Commun., 1983, 862; M. Yoshifuji, K. Ando, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, Angew. Chem., Int. Ed. Engl., 22, 418 (1983).
11) M. Yoshifuji, K. Shibayama, N. Inamoto, and T. Watanabe, Chem. Lett., 1983, 585.
12) M. Yoshifuji and N. Inamoto, Tetrahedron Lett., 24, in press (1983).
13) E. Fluck and K. Issleib, Z. Anorg. Allg. Chem., 339, 274 (1965).
14) M. Yoshifuji, K. Toyota, K. Shibayama, and N. Inamoto, Chem. Lett., 1983, 1653.
15) L. Maier, Chem. Ber., 94, 3043 (1961); J. Inorg. Nucl. Chem., 24, 275 (1962).
16) H. C. E. McFarlane and W. McFarlane, J. Chem. Soc., Chem. Commun., 1971, 1589.
17) R. K. Harris and R. G. Hayter, Can. J. Chem., 42, 2282 (1964).
18) M. Yoshifuji, I. Shima, K. Ando, and N. Inamoto, Tetrahedron Lett., 24, 933 (1983).

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