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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.

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

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

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

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, $PrC\underline{H}_2P^b$), 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 $\underline{Pr}CH_2P^b$); 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).

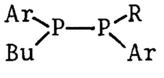
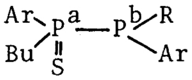
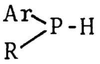
Table 1 shows the ^{31}P NMR data of the phosphorus compounds (3 - 5) thus obtained. The diphosphanes 3 showed complicated spectra in some cases, however, monosulfides 4 gave a simple AB quartet pattern. The further sulfurization in the presence of excess sulfur failed to give diphosphane disulfides,[15] 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 $>P^+=\overset{\vee}{P}-S^-$.[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 $(Cl-P=S)_n$, 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	 (3) δ_P(THF)/ppm[a] (J_{PP}/Hz)	 (4) δ_P(CDCl$_3$)/ppm (J_{PP}/Hz) a b	Yield %[d]	Mp °C	 (5) 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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