

Syntheses and Spectra of Asymmetric Diphosphine Disulfides

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Diphenylphosphine reacted with dialkylphosphinous chlorides followed by treatment with elemental sulfur to give the new compounds, P,P-Dialkyl-P',P'-diphenyl Diphosphine Disulfides; $\text{Ph}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$ (I), $\text{Ph}_2\text{P}(\text{S})\text{P}(\text{S})\text{Et}_2$ (II), and $\text{Ph}_2\text{P}(\text{S})\text{P}(\text{S})\text{Pr}_2^n$ (III). From the ^1H NMR spectra of I, the coupling constants; $J_{\text{P-C-H}}$ and $J_{\text{P-P-C-H}}$ were determined.

The ^{31}P NMR revealed the phosphorus atoms having phenyl groups resonated at a higher magnetic field than those having alkyl groups. Another spectroscopic data were also analyzed to give some important information concerning organophosphorus compounds.

1 Introduction

Although there is a considerable current interest in the compounds containing the phosphorus-phosphorus bond,¹⁾ relatively few synthetic attempts have been carried out on the asymmetrically substituted diphosphine disulfides compared to those of symmetric diphosphine disulfides. Issleib et al. reported the synthesis and ^{31}P NMR spectra of $\text{R}_2\text{P}(\text{S})\text{P}(\text{S})\text{R}'_2$ ($\text{R}=\text{Ph}$ or Et , $\text{R}'=\text{cyclo-C}_6\text{H}_{11}$ or Et), and found the chemical shifts of phosphorus atom in these compounds were ranged at $-20\sim-50$ ppm from 85% H_3PO_4 .^{2),3)} Further attempts to analyze spectroscopic data of compounds of this type will give much information regarding the structure of organophosphorus compounds because of their asymmetric structure. In this publication, ^1H and ^{31}P NMR spectra, IR spectra and Mass spectra of P, P-Dialkyl-P', P'-diphenyldiphosphine disulfides (I, II and III) along with the synthesis of them (new compounds) were reported.

2 Experimental

2.1 Measurements:

The measurement of ^{31}P NMR spectra was performed on JNM C-60 HL ^{31}P unit (24 MHz) by using JNM SD-HC as a heteronuclear spin decoupler and IS-60 as a proton irradiation sweep unit. The ^1H NMR spectra were obtained by using JNM 4H-100 instrument, along with JNM SD-HC ^{31}P OSC unit (48 MHz). IR spectra were obtained by Nippon Bunko IR 403G spectrometer using KBr pellets. Mass spectra were measured on JMS-OISG equipped with a heated inlet system operating at 160 °C.

2.2 Preparations:

P, P-Dimethyl-P', P'-diphenyldiphosphine disulfide (I) was prepared according to the

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usual salt formation method. Equimolar amounts of dimethylphosphine chloride and diphenylphosphine in ether were mixed under the presence of triethylamine at -5°C . To this reaction mixture, powdered sulfur was added at room temperature, and the mixture was heated under reflux for 3 hrs. Removal of precipitates (Et_3NHCl) and excess sulfur gave crude disulfide (I), which was found to contain tetramethyldiphosphine disulfide and tetraphenyldiphosphine disulfide by comparison of the NMR and IR spectra with those of authentic samples.^{4),5)} The disulfide (I) was purified by column chromatography on silica gel using benzene-ethanol (95:5 Wt) and obtained in 40% yield based on the reagents used, mp 112.7°C . Found: C, 53.91; H, 5.18; P, 19.47%. Calcd for $\text{C}_{14}\text{H}_{18}\text{P}_2\text{S}_2$: C, 54.18; H, 5.20; P, 19.16%. P,P-Diethyl-P',P'-diphenyldiphosphine disulfide (II) and P,P-di-n-propyl-P',P'-diphenyldiphosphine disulfide (III) were prepared by similar method in 30 and 25% yield, respectively. II had mp $121.7\text{--}121.8^{\circ}\text{C}$ (Lit.⁶⁾ $110\text{--}112^{\circ}\text{C}$). Found: C, 56.93; H, 6.26; P, 18.30%. III had mp $133.5\text{--}135.0^{\circ}\text{C}$. Found: C, 59.09; H, 6.55;

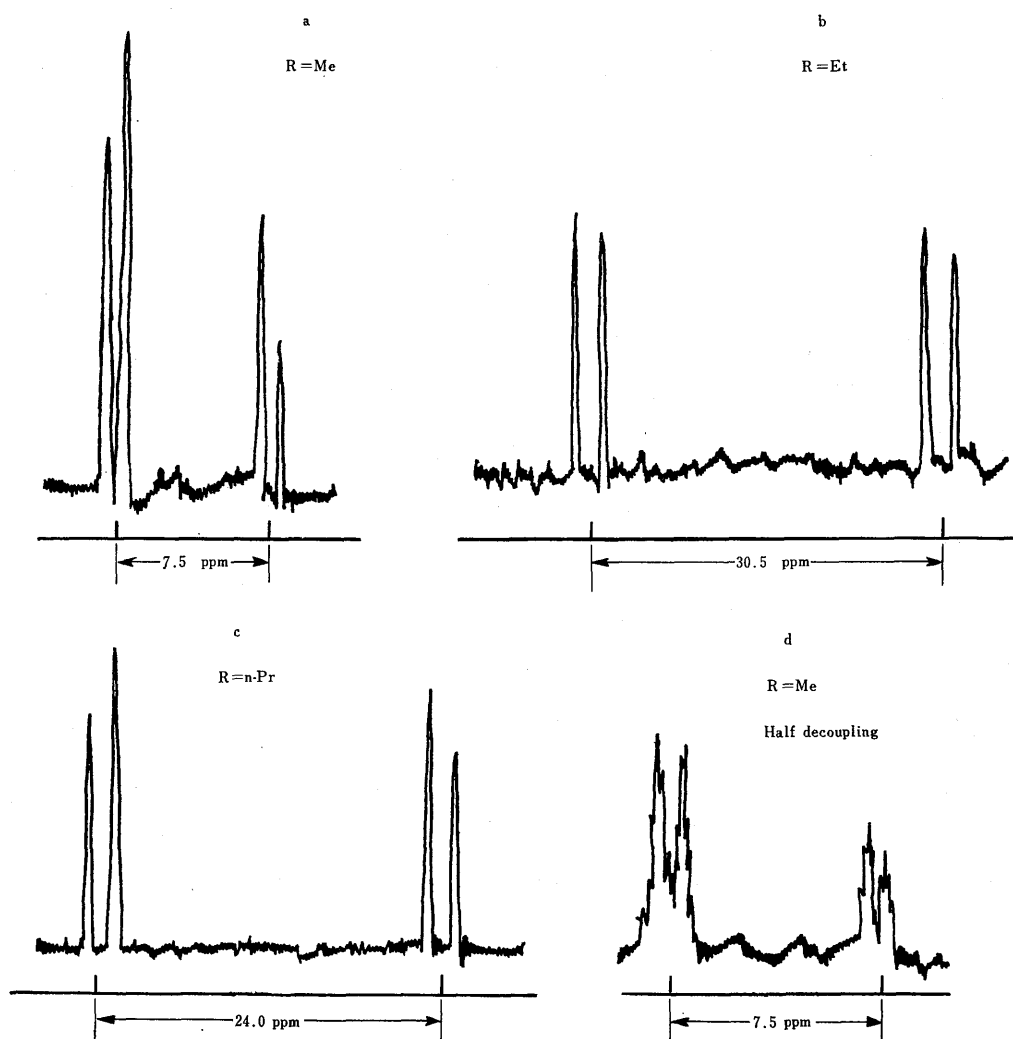


Fig. 1 $^{31}\text{P}\{-^1\text{H}\}$ NMR Spectra of $\text{R}_2\text{P}(\text{S})\text{P}(\text{S})\text{Ph}_2$ 20% in CDCl_3

P, 16.47%. Calcd for $C_{18}H_{24}P_2S_2$: C, 59.00; H, 6.60; P, 16.90%.

3 Result and Discussion

^{31}P NMR spectra obtained by perfect decoupling of all protons attached to the phosphorus atoms are depicted in Figs. 1a~1c. Fig. 1d shows the result of half decoupling

Table 1 ^{31}P Chemical Shifts and Coupling Constants of $\text{R}_2\text{P}(\text{S})\text{P}(\text{S})\text{Ph}_2$

	R	δ (^{31}P) from 85% H_3PO_4 (ppm)		$J_{\text{P-P}}$ (Hz)
		PPh_2	PR_2	
I	Me	-32.4	-40.1	22.5
II	Et	-27.5	-57.7	39.6
		-26.0 ^{a)}	-57.7 ^{a)}	...
III	n-Pr	-27.8	-51.5	39.6

a) See ref. 3.

of the protons attached to I. The chemical shifts (from 85% H_3PO_4) and coupling constants ($J_{\text{P-P}}$) of I, II and III are shown in Table 1. The doublet of septets (A in Fig. 1d) can be attributed to a spin-spin coupling between the phosphorus atom and methyl protons attached directly to the phosphorus atom. Moreover the Nuclear Overhauser effect⁷⁾ results in an enhancement of intensity of the peaks appeared at low field (Fig. 1a~1d). In this case, the phosphorus atoms whose peaks are enhanced by the Nuclear Overhauser effect has the alkyl group on them, and the proton nuclei are situated at β -position. On the other hand, the phosphorus atoms which have the phenyl groups on them have the proton nuclei at γ -position. The unfair surrounding around the phosphorus atoms causes unequal intensity in their NMR resonance. These facts lead the conclusion that the phosphorus atom bonded to the phenyl groups resonates at higher field than that bearing the alkyl substituents consisting with the Shoolery's rule.¹⁵⁾ The δ (^{31}P) values of $\text{Et}_2\text{P}(\text{S})\text{P}(\text{S})(\text{cyclo-C}_6\text{H}_{11})_2$ have been reported to be -47.6 and -57.1 ppm without attributing to any special phosphorus atom.⁸⁾ From these figures, we can assume the alkyl substituents on the phosphorus atom cause a high field shift in the ^{31}P NMR. The coupling constants ($J_{\text{P-P}}$) of the compounds I, II and III are rather small compared to that (69 Hz) of the same compounds mentioned above which has been the only $J_{\text{P-P}}$ of asymmetric diphosphine disulfide known so far. The coupling constant is known to have regular relations with the substituents and the bond order between two nuclei.¹⁶⁾ In this case, the phenyl groups reduce the electron density on one of the two phosphorus atoms and decrease the bond order of the phosphorus-phosphorus bond because of the sp^2 property of the carbon atoms of phenyl groups.

Fig. 2 shows the results of ^1H NMR spectra of I. In a single resonance spectrum (Fig. 2a), there are a quartet at τ 8.08 ppm and complex multiplets at τ 1.40-2.45 ppm. When the system is irradiated by the resonance frequency of 40.481302 MHz which corresponds to the resonance frequency of the phosphorus atom bearing methyl groups

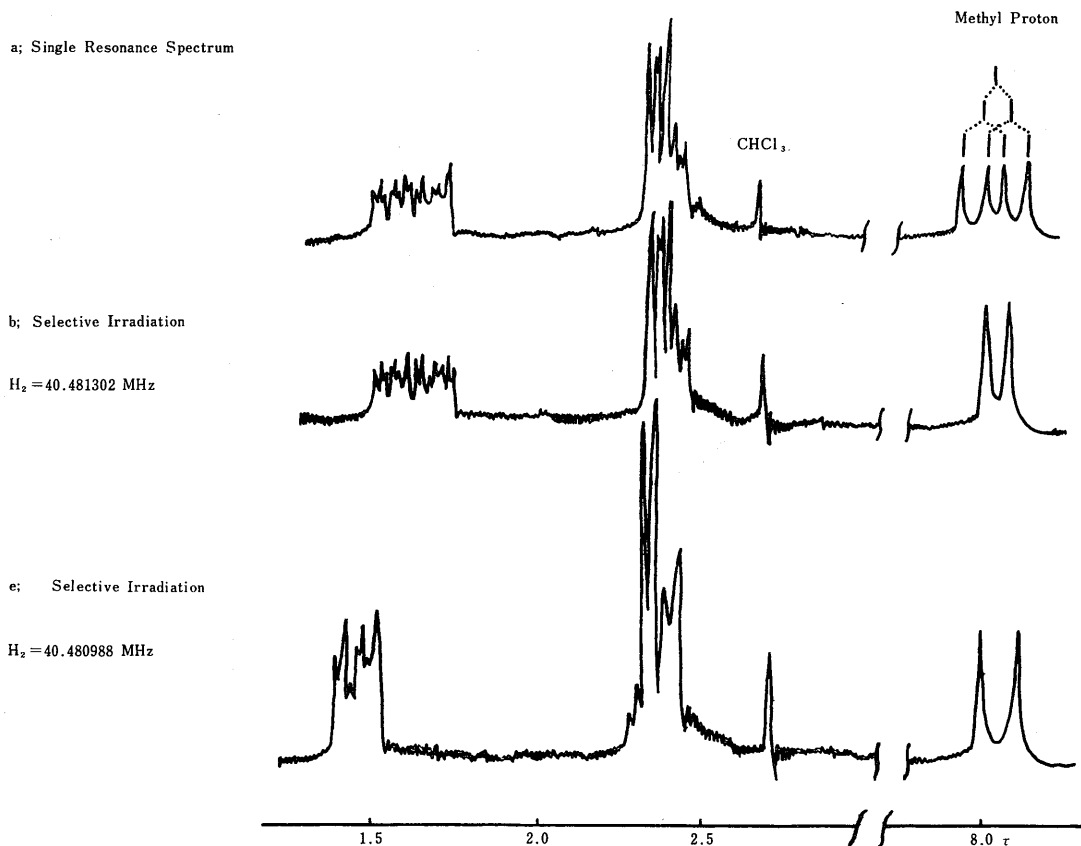
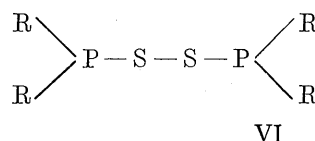
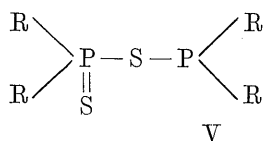
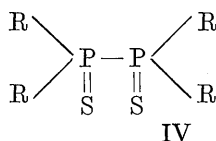


Fig. 2 ^1H NMR Spectra of $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Ph}_2$ 20% in CDCl_3

(Fig. 2b), the signals of the methyl protons (τ 8.08) collapse into a doublet whose coupling constant was about 7Hz, and also by the resonance frequency of 40.480988 MHz (Fig. 2c), the same change is observed, except that the coupling constant is about 13 Hz, and the narrowing of the multiplets which come from the ortho-proton of the phenyl groups. Therefore the four peaks of methyl proton can be assigned as shown in Fig. 1a, and the exact coupling constant, $J_{\text{P-C-H}}$ and $J_{\text{P-P-C-H}}$ are calculated to be 13.0 and 7.8 Hz, respectively. This phenomenon contrasts with the empirical facts that in the organophosphorus compounds, the $J_{\text{P-C-C-H}}$ is always bigger than $J_{\text{P-C-H}}$.

Regarding the structure of tetraalkyldiphosphine disulfide, the following three structures are possible.



However, it has been shown by X-ray crystallography that $\text{Me}_4\text{P}_2\text{S}_2$,⁹⁾ $\text{Et}_4\text{P}_2\text{S}_2$,⁹⁾ and $\text{MeEtP}(\text{S})\text{P}(\text{S})\text{MeEt}$ ¹⁰⁾ have the structure of type IV. Moreover, it was shown that $\text{Me}_4\text{P}_2\text{S}_2$ possessed a center of symmetry and also the vibrational frequencies ascribed to $\text{P}=\text{S}$ stretching.^{4), 11)} Mass spectra of $\text{Me}_4\text{P}_2\text{S}_2$ also have showed fragments that

Table 2 IR Spectra of $R_2P(S)P(S)Ph_2$ ^{a)} (cm^{-1})

$Me_2P(S)P(S)Ph_2$	$Et_2P(S)P(S)Ph_2$	$n-Pr_2P(S)P(S)Ph_2$	Assignment
1450(s)	1445(m)	1433(m)	P-Ph
1273(m)	1277(m)	1274(m)	P-CH ₂ -
1160(w)	1158(w)	1181(s)	Ph deform.
	1091(s)	1160(m)	in plane
1097(s)	1046(m)	1087(vs)	
1024(w)	1023(s)	1074(m)	
974(s)	930(w)	995(m)	
907(s)		861(w)	CH ₃ rock.& wag.
856(w)	854(w)	843(m)	
749(s)	763(s)	750(vs)	P-C asym. or
	751(vs)	715(s)	Ph deform. out of plane
731(s)	743(s)	711(s)	P=S Band I
713(s)	710(s)	697(s)	
695(m)	689(vs)	689(vs)	Ph deform. out of plane
688(s)	673(m)		
647(s)	642(vs)	647(m)	
590(vs)	610(s)	610(s)	P=S Band II
	578(S)	596(vs)	
	419(s)	489(vs)	
	480(s)	470(m)	
	455(m)		
447(w)	447(w)	449(w)	P-P

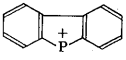
a) Measured as KBr pellets

have two P atoms without any sulfur atom.¹¹⁾ All these observations suggest that tetraalkyldiphosphine disulfides have the structure of type IV.

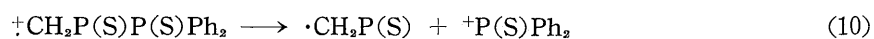
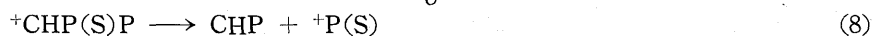
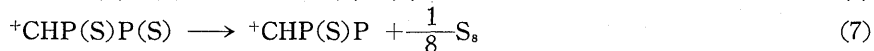
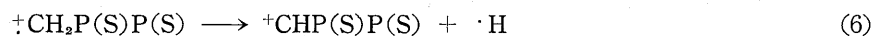
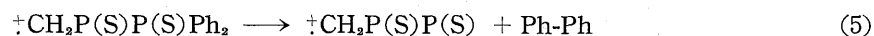
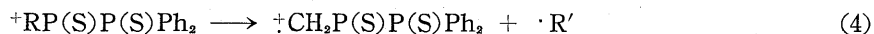
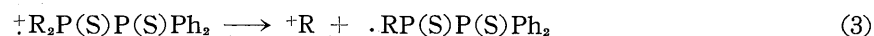
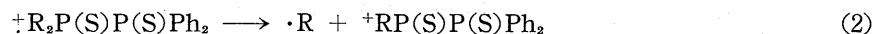
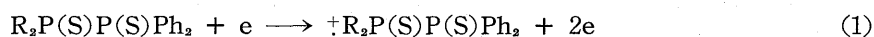
The IR data (in Table 2) show the weak absorptions at 447-449 cm^{-1} which can be ascribed to P-P stretching frequencies. The P-P stretching frequencies of symmetric diphosphine disulfides were reported at 437 cm^{-1} (P_2H_4),¹¹⁾ 424 cm^{-1} (Et_4P_2),¹²⁾ 419 cm^{-1} (Bu_4P_2),¹⁸⁾ and 445 cm^{-1} ($Me_4P_2S_2$)¹¹⁾ in Ramann Spectra. The strong IR bands at 711-743 cm^{-1} (Band I), and 590-610 cm^{-1} (Band II) can be assigned to P=S stretching frequencies.¹⁴⁾ Therefore, judging from these points, the direct P-P linkage can be assumed for I, II, and III. The bands at 1433-1451 cm^{-1} are the absorptions characteristic of P-Ph groups, and those of P-CH₂- groups are observed at 1274-1276 cm^{-1} .

The mass spectra (Table 3) of I, II and III are somewhat different from those of $Me_4P_2S_2$ observed by Cowley et al..¹¹⁾ They got the peak fragment which had two phosphorus atom without sulfur atom. In our experiments, the corresponding peaks are not obtained, but there are strong parent peaks along with P+1, and P+2. The peak at m/e 183 is

Table 3 Mass Spectra of $R_2P(S)P(S)Ph_2$

$Me_2P(S)P(S)Ph_2$		$Et_2P(S)P(S)Ph_2$		$n-Pr_2P(S)P(S)Ph_2$		Fragments
m/e	%	m/e	%	m/e	%	
310	100	338	100	366	100	P
311	21.4	339	21.4	367	21.6	P+1
312	14.6	340	13.6	681	13.5	P+2
—	—	—	—	323	8.7	$^+PrP(S)P(S)Ph_2$
—	—	309	25.8	—	—	$^+EtP(S)P(S)Ph_2$
217	100	217	100	217	23.1	$^+CH_2P(S)P(S)Ph_2$
185	3.6	185	4.5	185	2.2	$^+PPh_2$
183	31.0	183	42.4	183	23.0	
140	2.0	140	4.3	140	1.5	$^+CH_2P(S)P(S)$
139	55.0	139	81.5	139	19.1	$^+CHP(S)P(S)$
107	17.2	107	34.1	107	100	$^+CHP(S)P(S)$
77	16.1	77	40.1	77	17.6	$^+CH_2PP(S)$
63	17.9	63	61.0	63	27.5	$^+P(S)$
—	—	—	—	47	74.9	^+Pr
—	—	29	41.3	—	—	^+Et

assumed to be dibenzoheterocyclic cation. The formation of this cation is very common in organophosphorus compound carrying phenyl groups on it,¹⁷⁾ and substantiated by finding the small metastable peak of its precursor at m/e 185. The other fragments can be explained by assuming the simple degradation of the compounds as shown in the following equations.



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