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PREPARATION AND CHARACTERIZATION OF SOME UNSYMMETRICAL THIADIPHOSPHIRANES

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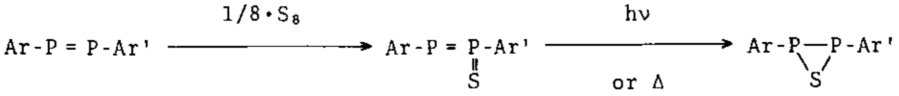
Abstract——Unsymmetrical diphosphenes 1b - d were monosulfurized and thermally or photochemically cyclized successively to give the corresponding unsymmetrical thiadiphosphiranes 3b - d. The spin-spin coupling constants $^1J_{PP}$ in the thiadiphosphirane ring system were directly observed for the first time.

Phosphorus containing small ring compounds are interesting because of their unusual physical and chemical properties.[1,2] Baudler *et al.* reported the preparation of 2,3-di-*tert*-butyl-1,2,3-thiadiphosphirane,[3] however, it was not stable enough to permit detailed structure analyses.

We recently reported the preparation and characterization of a sterically protected very stable thiadiphosphirane, *E*-2,3-bis(2,4,6-tri-*tert*-butylphenyl)-1,2,3-thiadiphosphirane (3a) starting from 2,4,6-tri-*tert*-butylphenylphosphonothioic dichloride and magnesium and the X-ray analysis of 3a was also carried out.[4] However, there has been no report on the spin-spin coupling constant, $^1J_{PP}$, in the ^{31}P NMR of the thiadiphosphirane ring system.

We now report[5] the preparation and characterization of some stable unsymmetrical thiadiphosphiranes 3b - d. The preparative methods for them involve monosulfurization of unsymmetrical diphosphenes 1b - d[6,7] followed by the successive cyclization



1a - d 2a - d 3a - d

a - c: Ar = 2,4,6-$Bu^t_3C_6H_2$; a, Ar' = Ar; b, Ar' = 2,4-Bu^t_2-6-MeC_6H_2;
c, Ar' = 2,4,6-$Me_3C_6H_2$.
d: Ar = [η^6-$Cr(CO)_3$]-2,4,6-$Bu^t_3C_6H_2$, Ar' = 2,4,6-$Bu^t_3C_6H_2$.

of the corresponding unsymmetrical diphosphene monosulfides 2b - d, as alternatively employed for the preparation of the symmetrical 3a.[8]

The procedure for the preparation of 2-mesityl-3-(2,4,6-tri-*tert*-butylphenyl)-1,2,3-thiadiphosphirane (3c) was as follows. The diphosphene 1c[6] (160.9 mg, 0.377 mmol), prepared from 2,4,6-tri-*tert*-butylphenylphosphine and mesitylphosphonous dichloride, was mono-sulfurized with elemental sulfur (1.2 equiv.) in benzene (1.5 ml) at room temperature overnight in the dark to give 2c in 38% yield after purification through silica gel column chromatography (in contrast to the preparations of 2a[8] and 2d, the reactions of 1b and 1c in the presence of triethylamine gave intractable materials). 2c: yellow, mp 91 - 95 °C; MS m/z 458 (M^+); $^{31}P\{^1H\}$ NMR (C_6H_6 from external 85% H_3PO_4 at 36.3 MHz) appeared as an AB pattern centered at δ_P 241.9 and 226.7 ppm with $^1J_{PP}$ = 604.3 Hz. The mono-sulfurization seemed to occur on the less hindered phosphorus atom according to the reasonable assignments of the ^{31}P, ^{13}C, and ^1H NMR spectra (Table 1). The mono-sulfide 2c (65.7 mg, 0.143 mmol) was irradiated with a medium pressure mercury lamp in the solid state at 0 °C for 5 min to afford 3c almost quantitatively. 3c: mp 46 - 48 °C; HR-MS m/z 458.2359, calcd for $C_{27}H_{40}P_2S$: 458.2326; $^{31}P\{^1H\}$ NMR (C_6H_6) δ_P -84.0 and -81.9 ppm (AB pattern with $^1J_{PP}$ = 232.9 Hz), where a negative values indicate upfield shifts relative to the standard, however, $^{31}P\{^1H\}$ NMR in $CDCl_3$ at 30 °C appeared as a singlet at δ_P -82.1 ppm. Similar solvent effect was observed in the case of the mono-sulfide 2a.[8] The configurational assignment of 3 has not been done except for 3a (X-ray analysis).[4] However, taking the steric hindrance within the molecule into account, 3b - d are reasonably assumed to take *E* form. The thiadiphosphirane 3c thus obtained was less stable than 3a and it liquefied on standing overnight at room temperature when exposed to air probably due to less effective steric protection, while 3a does not decompose over the period more than a year under the same conditions. Very similarly the thiadiphosphiranes 3b and 3d were prepared from the corresponding unsymmetrical diphosphenes 1b[6] and 1d[7] *via* the mono-sulfides 2b and 2d, respectively. 2b: mp 129 - 131 °C; HR-MS m/z 542.3265, calcd for $C_{33}H_{52}P_2S$: 542.3265. 3b: mp 80 - 82 °C; MS m/z 542 (M^+). The yield of 3b was also almost quantitative from 2b. $^{31}P\{^1H\}$ NMR of 3b appeared as an AB pattern either in $CDCl_3$ or in C_6H_6 at 30 °C (Table 2). 2d: FD-MS (at room temperature) m/z 721 ($M^+ + 1$). 3d: mp 134 - 136 °C; IR (KBr) ν_{CO} 1958, 1888 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ϵ) 325 (7700); MS m/z 720. The reaction of 1d with sulfur in triethylamine was very fast and was completed within 2 h. During the photocyclization of 2d to 3d, no decomplexation of the chromium part

Table 1.   Some Spectroscopic Data of Diphosphene Mono-sulfides 2

2	^{31}P NMR Parameters				IR (KBr)	UV (CH_2Cl_2)	MS (M^+)	Yield[g]
	δ_P/ppm		$^1J_{PP}$/Hz	Solv.	ν_{PP}, ν_{PS}/cm^{-1}	λ_{max}/nm (ε)	m/z	%
2a[a]	255.8	247.8	629.9	Et_3N	740, 624	267 (18300) 384 (6650)	584.3755	67
2b[b]	249.1	239.3	625.0	C_6H_6	720, 618	253 (19000) 373 (7800)	542.3265	22
2c[c]	241.9	226.7	604.3	C_6H_6	737, 637	244 (13800) 267sh (8700) 368 (2990)	458	38
2d[d]	254.1	247.7	666.5	$CDCl_3$	716, 620[e]	262 (16400) 325 (7970) 378 (9830)	721[f]	73[h]

a) Taken from Ref. (8), 2a: $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 123.4 (t, *J* = 5.4 Hz, m-Ar'), 123.3 (s, m-Ar). *b*) 2b: ^1H NMR ($CDCl_3$) δ 7.50 (pseudo-t, 2H, *J* = 1.8 Hz, arom.-Ar), 7.47 + 7.15 (br.s, 1H + 1H, arom.-Ar'), 2.83 (s, 3H, o-Me), 1.68 (s, 9H, o-Bu^t-Ar'), 1.61 (s, 18H, o-Bu^t-Ar), 1.35 + 1.32 (s + s, 9H + 9H, p + p'-Bu^t); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 126.5 (dd, *J* = 3.7 and 5.6 Hz, m-Ar'), 123.6 (s, m-Ar), 122.9 (dd, *J* = 4.4 and 6.3 Hz, m-Ar'). *c*) 2c: ^1H NMR ($CDCl_3$) δ 7.52 (s, 2H, arom.-Ar), 6.94 (s, 2H, arom.-Ar'), 2.65 (s, 6H, o-Me), 2.30 (s, 3H, p-Me), 1.62 (s, 18H, o-Bu^t), 1.35 (s, 9H, p-Bu^t). *d*) 2d: ^1H NMR ($CDCl_3$) δ 7.48 (dd, 2H, *J* = 2.31 and 3.63 Hz, arom.-Ar), 6.14 (s, 2H, arom.-Ar'), 1.68 + 1.63 (s + s, 18H + 18H, o + o'-Bu^t), 1.36 + 1.31 (s + s, 9H + 9H, p + p'-Bu^t); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 123.8 (dd, *J* = 3.3 and 8.1 Hz, m-Ar'), 95.5 (s, m-Ar). *e*) ν_{CO} [$Cr(CO)_3$] 1955, 1886 cm^{-1}. *f*) FD-MS at room temperature (M^+ + 1). *g*) Isolated yields from the diphosphenes 1. *h*) 3d was also obtained in 15% yield.

Table 2. ^{31}P NMR Parameters and Mass Spectral Data of Thiadiphosphiranes 3

3	^{31}P NMR Parameters in Chloroform and in Benzene								MS (M^+)
	δ_P/ppm		$^1J_{PP}$/Hz	Solv.	δ_P/ppm		$^1J_{PP}$/Hz	Solv.	m/z
3a	-65.1[a]		---	$CDCl_3$	-66.6		---	C_6H_6	584
3b[b]	-67.0	-72.5	245.4	$CDCl_3$	-66.2	-73.6	244.1	C_6H_6	542
3c[c]	-82.1		---	$CDCl_3$	-81.9	-84.0	232.9	C_6H_6	458.2359
3d[d]	-46.9	-60.0	271.0	$CDCl_3$	-46.9	-60.0	271.0	C_6H_6	720

a) Taken from Ref. (4). *b*) 3b: ^{1}H NMR ($CDCl_3$) δ 7.13 (d, 2H, $^4J_{PH}$ = 1.3 Hz, arom.-Ar), 7.13 + 6.93 (m + m, 1H + 1H, arom.-Ar'), 2.59 (d, 3H, $^4J_{PH}$ = 4.8 Hz, Me), 1.68 (s, 9H, o-Bu^t-Ar'), 1.63 (d, 18H, $^5J_{PH}$ = 0.7 Hz, o-Bu^t-Ar), 1.27 (s, 18H, p + p'-Bu^t). *c*) 3c: ^{1}H NMR ($CDCl_3$) δ 7.14 (s, 2H, arom.-Ar), 6.77 (s, 2H, arom.-Ar'), 2.62 (s, 6H, o-Me), 2.21 (s, 3H, p-Me), 1.67 (s, 18H, o-Bu^t), 1.26 (s, 9H, p-Bu^t). *d*) 3d: ^{1}H NMR ($CDCl_3$) δ 7.13 (d, 2H, $^4J_{PH}$ = 1.5 Hz, arom.-Ar), 6.07 (s, 2H, arom.-Ar'), 1.63 + 1.60 (s + s, 18H + 18H, o + o'-Bu^t), 1.26 (s, 9H + 9H, p + p'-Bu^t).

was observed. The thermal cyclization of 2d seemed to be very fast, since 15% yield of 3d was obtained already during the preparation of 2d (73% yield) and during the mp measurement of 2d.

It should be noted that the spin-spin coupling constants $^1J_{PP}$ were first directly observed for the unsymmetrical thiadiphosphiranes 3b - d (Table 2) and that for 3d (271.0 Hz) is extraordinarily large among those reported for the three-membered diphospha-ring system compounds measured by Baudler et al.[1]

Moreover, the coupling constants $^1J_{PP}$ in 2a - d (Table 1) are among the largest values ever observed for directly bonded phosphorus-phosphorus linkage,[9] because of the existence of the double bond character[10] of current interest.[6-8, 11-15]

It is also noteworthy that the chemical shifts appear in a very similar region in spite of the difference in coordination numbers of both the phosphorus atoms in diphosphene mono-sulfides 2.

Further theoretical studies on these reaction pathways involving mono-sulfurization and isomerization (1 → 2 → 3) are in progress.

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