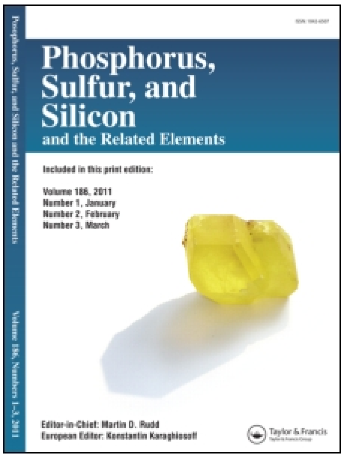


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTIVITY OF METHYLENETRIPHENYLPHOSPHORANES HAVING TWO PHENYL GROUPS CONSTRAINED WITH ETHANO OR ETHENO BRIDGE

Yasuhiko Kawamura[a]; Yasunori Iwano[a]; Noboru Watanabe[a]; Tokunaru Horie[a]; Masao Tsukayama[a]
[a] Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, Tokushima, Japan

To cite this Article Kawamura, Yasuhiko , Iwano, Yasunori , Watanabe, Noboru , Horie, Tokunaru and Tsukayama, Masao(1998) 'REACTIVITY OF METHYLENETRIPHENYLPHOSPHORANES HAVING TWO PHENYL GROUPS CONSTRAINED WITH ETHANO OR ETHENO BRIDGE', Phosphorus, Sulfur, and Silicon and the Related Elements, 132: 1, 167 — 181

To link to this Article: DOI: 10.1080/10426509808036985

URL: http://dx.doi.org/10.1080/10426509808036985

Phosphorus, Sulfur and Silicon, Vol. 132, pp. 167-181
Reprints available directly from the publisher
Photocopying permitted by license only

REACTIVITY OF METHYLENETRIPHENYLPHOSPHORANES HAVING TWO PHENYL GROUPS CONSTRAINED WITH ETHANO OR ETHENO BRIDGE

YASUHIKO KAWAMURA*, YASUNORI IWANO,
NOBORU WATANABE, TOKUNARU HORIE and
MASAO TSUKAYAMA

Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, Minamijosanjima-cho, Tokushima 770, Japan

(Received 6 December, 1997; In final form 22 October, 1997)

Methylenetriphenylphosphoranes having two phenyl groups tied together with ethano or etheno bridge were prepared by conventional ways in order to suppress delocalization of an ylide-carbanion by deforming geometrical arrangement of phenyl groups from that of the diarylmethylene derivative and hence to elevate reactivities of diarylmethylenephosphoranes. These P-ylides were, however, still unreactive with usual aldehydes and ketones. The reasons are deliberated by molecular orbital calculations and the ^{31}P-NMR data. The HOMO orbitals of ethano-bridged and etheno-bridged diarylmethylenephosphoranes are located on a monoarylcarbanion and a carbanion, respectively. Although these tendencies are auspicious to enhance the Wittig reactivity of them, the electron densities of the ylidic carbons are still insufficient. ^{31}P-NMR chemical shifts of the ylides revealed that the objective P-ylides do not have a large extent of the ylide-contribution in the ylide-yllene resonance. Meanwhile, they reacted readily with tetrahalo *o*-quinones to give 1,3-dioxoles in good yields. Thermochromic behavior of one of the precursors, dibenzosuberenylphosphonium salt, was observed at 80 °C in acetonitrile in the presence of trace perchloric acid. The colored species is elucidated as dibenzo[a,e]tropylium cation.

Keywords: Phosphorus ylide; diarylmethylenephosphorane; ^{31}P NMR; 1,3-dioxole; thermochromism

---

* Corresponding author.

INTRODUCTION

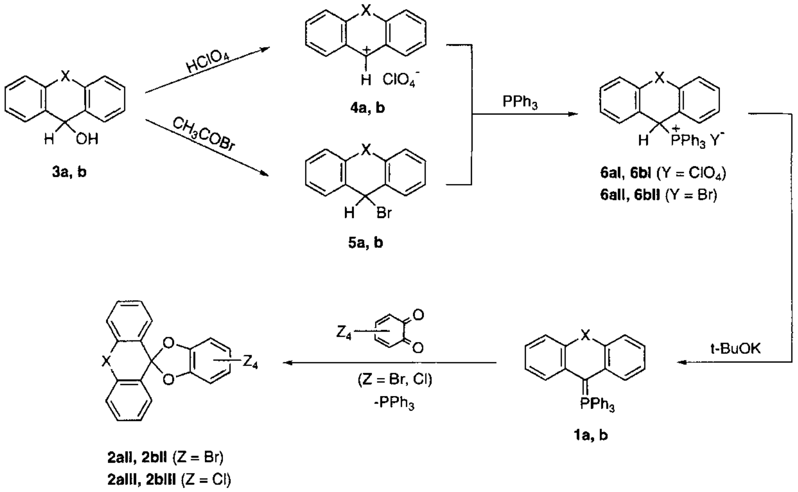
Diarylmethylenephosphoranes known to be stable P-ylides, usually need forcing reaction conditions to induce the Wittig reaction.[1] Johnson and LaCount have described that the Wittig reactivity of a congener P-ylide, fluorenylidenephosphorane depends upon an ylidic character of an ylide-yllene resonance of the phosphorane.[2] Actually, the ylide having an electron-donating *n*-butyl group on phosphorus showed higher Wittig reactivity than that having an aryl group on phosphorus.[2] Although a P-substituent effect on the Wittig reactivity has been thus discussed frequently, that of carbanion has been argued less so far, especially in diarylmethylenephosphoranes. We have been interested in exploiting new applications of stable ylides based on a conception that the ylides can be regarded as a good single electron-transfer reagent and/or a good redox reagent due to internal ionic nature.[3] In order to extend the novel redox chemistry of the stable P-ylides, it is essential to understand the carbanion-substituent effect on the stability and reactivity of P-ylides as well as the P-substituent effect on those. In principle, since delocalization of negative charge of carbanion in diarylmethylenephosphorane seems to play a crucial role on reactivity, we plan to examine four structurally intimate P-ylides, diphenylmethylene-,[4] fluorenylidene-[5] dibenzosuberanylidene-(**1a**), and dibenzosuberenylidenetriphenylphosphorane (**1b**).[6] In a simplified form, a fluorenylide ion is a 14π-electron system (Hückel rule), so that the corresponding P-ylide is expected to be very stable. By contrast, an anion of dibenzosuberene is a 16π-electron system, if the structure is planar. Hence, the stability is lowered and the higher reactivity is expected. The situation, however, seems not to be so simple, because of an ylide-yllene resonance and mutual interaction between diaryl group and substituents on phosphorus. We wish to report herein the results of the study directing the above theme.

RESULTS AND DISCUSSION

Since dibenzosuberanylidenetriphenylphosphorane (10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidenetriphenylphosphorane ; **1a**) is unknown and dibenzosuberenylidenetriphenylphosphorane

(5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidenetriphenylphosphorane; **1b**) is known[6] but detailed physical property is unavailable in literature, preparations and identifications of two ylides are described first.

Each precursor, a phosphonium salt, was prepared as a perchlorate (**6aI** and **6bI**) and a bromide (**6aII** and **6bIII**) by the procedure shown in SCHEME 1. Preparations of **1a** and **1b** *via* **6aI** and **6bI** involved generation of the corresponding salts (**4a** and **4b**), which reacted with triphenylphosphine and followed by deprotonation. Meanwhile, compounds **6aII** and **6bII** were prepared by the bromination of the starting alcohol (**3a** and **3b**) with acetyl bromide[7] and followed by the reaction with triphenylphosphine. In deprotonation, treatment of **6** with a base such as sodium ethoxide gave ylides with insufficient purity presumably due to hydrolysis by trace amount of water. Instead, pure **1a** as orange and **1b** as red crystals were obtained using potassium *t*-butoxide in dry benzene-ether under anaerobic conditions. The ylides as well as the phosphonium salts obtained here are characterized as shown in TABLEs I-III. From the point of stability, **1a** and **1b** survive for a week when both are stored as solids under ordinary laboratory conditions. Condensation of the ylides with several carbonyl compounds was then investigated, but the usual aliphatic and aromatic aldehydes and ketones were totally unreacted.



a: X = -CH$_2$CH$_2$-; b: X = -CH=CH-
I: Y = ClO$_4$; II: Y or Z = Br; III: Z = Cl

SCHEME 1

TABLE I Physical data of dibenzosuberanyl- (**6a**) and dibenzosuberenyltriphenylphosphonium (**6b**) salts

Compd	*mp/°C*	*Yield/%*	*^{1}H NMR^{a} δ/ppm*	*Molecular Formula^{b}*	*IR (KBr) ν/cm^{-1}*
6aI	223–224	83	2.75 (2H, s), 2.76 (2H, s), 6.25 (1H, d, 21), 7.02 (2H, t, 8), 7.1-7.3 (12H, m), 7.57 (6H, td, 8, 4), 7.78 (3H, t, 7)	$C_{32}H_{28}O_4ClP$	1590w, 1500m, 1490m, 1450s, 1095vs, 1000s,760s, 700s
6aII	207–210	86	2.72 (2H, s), 2.73 (2H, s), 6.81 (1H, d, 21), 6.99 (2H, t, 7), 7.12(2H, d, 7), 7.24 (2H, t, 8), 7.25 (3H, d, 3), 7.28 (3H, d, 7), 7.49(2H, brd, 8), 7.56 (6H, td, 9, 3), 7.77 (3H, t, 8)	$C_{33}H_{28}BrP$	1590w, 1490w, 1450s, 1110s, 1100s, 1000m,775s, 760s, 690s
6bI	233–234	83	6.19 (2H, s), 6.48 (1H, d, 18), 7.2–7.3 (10H, m), 7.35 (2H, tt, 7,2), 7.52 (6H, td, 8, 4), 7.61 (2H, d, 8), 7.73 (3H, t, 7)	$C_{33}H_{26}O_4ClP$	1590w, 1490w, 1440s, 1100vs, 1000m, 810s,750s, 685s
6bII	219–220	86	6.11 (2H, s), 7.18 (2H, m), 7.31 (4H, t, 4), 7.4–7.6 (13H, m), 7.71(3H, t, 7), 8.29(2H, d, 7)	$C_{33}H_{26}BrP$	1600w, 1510w, 1495w, 1450s, 1110s, 1000m,820s, 770s, 690s

a Measured in $CDCl_3$ at 400 MHz. s, Singlet; d, doublet; t, triplet; m, multiplet; br, broad. Coupling constants (Hz) are shown in paretheses.

b Satisfactory microanalyses were obtained: C,H ± 0.3.

TABLE II Physical data of dibenzosuberanylidene- (**1a**) and dibenzosuberenylidenetriphenylphosphorane (**1b**)

Compd	*mp/°C*	*Yield/%*	*Molecular Formula*[a]	*^{31}P NMR*[b]	*IR (KBr) ν/cm^{-1}*	*UV-VIS λ_{max}/nm (log ε)*[c]
1a	143–145	83	$C_{33}H_{27}P$	10.91	1440s, 1223w, 1202s,1100s, 999m	286 (4.04), 343 (3.25), 500 (end)
1b	115–116	73	$C_{33}H_{25}P$	10.36	1441s, 1218w, 1193m, 1098s, 1000m	286 (4.32), 345 (3.56), 520 (end)

a Satisfactory microanalyses were obtained: C, H ± 0.3.
b Measured in THF-d_8 at 162 MHz. Phosphoric acid (85%) was used as external standard.
c Measured in MeCN.

TABLE III ^{1}H NMR data of the phosphoranes (**1**) and the precursor phosphonium salts (**6**)[a]

Compd	*Ethano- or etheno bridge-H*	*Benzyl-H*	*Benzene ring-H*	*$\equiv P^+$-Ph*
6aI	2.74 (4H, s)	6.61 (1H, d, 22)	7.06 (2H, t, 7), 7.19 (2H, d, 7), 7.26 (2H, d, 7), 7.34 (2H, t, 7)	7.23 (6H, dd, 12, 8), 7.64 (6H, td, 8, 3), 7.89 (3H, t, 8)
6bI	6.29 (2H, s)	6.75 (1H, d, 19)	7.38 (2H, t, 8), 7.41 (2H, d, 8), 7.47 (2H, t, 8), 7.55 (2H, d, 8)	7.29 (6H, dd, 12, 8), 7.62 (6H, td, 8, 3), 7.87 (3H, t, 8)
1a	2.49 (4H, s)	----	6.36 (2H, t, 8), 6.43 (2H, t, 7), 6.57 (2H, d, 8), 6.79 (2H, d, 7)	7.47 (9H, br), 7.73 (6H, br)
1b	6.36 (2H, s)	----	6.37 (2H, d, 7), 6.47 (4H, m), 6.62 (2H, d, 7)	7.46 (6H, t, 7), 7.52 (3H, t, 7), 7.80 (3H, d, 7), 7.83 (3H, d, 7)

a Measured in DMSO-d_6 at 400 MHz. s, Singlet; d, doublet; t, triplet; m, multiplet ; br, broad.
Coupling constants (Hz) are shown in paretheses.

As an extension of the study of stable phosphoranes, *i.e.*, reactions of fluorenylidenetriphenylphosphorane and -arsinane with activated carbonyls by Boulos *et al.*, [8] we further exploited the reactivity of **1a** and **1b** with tetrahalo *o*-quinones (SCHEME 1), phthalic and maleic anhydrides, and thiobenzophenone. Thiobenzophenone failed to react with **1a** and **1b**. Although phthalic and maleic anhydrides reacted with **1a** and **1b**, the products could not be isolated and characterized, possibly due to their low stability. Tetrahalo *o*-quinones reacted readily with **1a** and **1b** to give the corresponding 1,3-dioxole (**2a, bII** and **III**) in favorable yields as shown in TABLE IV. This work, therefore, gives supplementary examples of the 1,3-dioxole formation of a stable phosphorus ylide with activated carbonyls reported by Boulos *et al.*,[8] and Bestmann and Lang.[9]

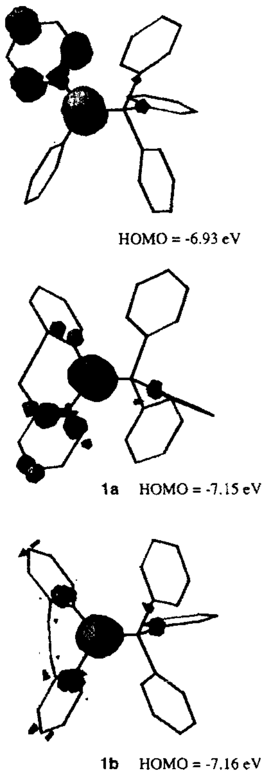


FIGURE 1 Energy optimized structures and HOMO orbitals of diphenylmethylenetriphenylphosphorane, and the phosphoranes, **1a** and **1b** (from top to bottom) calculated by the semiempirical PM3 SCF-MO method.[10]

TABLE IV Physical data of spiro[dibenzosuberane-] (**2a**) and spiro[dibenzosuberene- 1,1′-tetrahalobenzo-2,5-dioxole] (**2b**)

Compd	*mp/°C*	*Yield/%*	*^{1}H NMR*[a]*/δ ppm*	*Molecular Formula*[b]	*IR (KBr)/ν cm^{-1}*	*MS*[c]*/m/e (%)*
2aII	199–201	82	3.45 (4H, s), 7.23 (4H, m), 7.33 (2H, m), 7.77 (2H, m)	$C_{21}H_{12}O_2Br_4$	1443s, 1291m, 1278m, 1019s, 775s, 760s	620 (M+4, 2), 618 (M+2, 14), 616 (M, 21), 614 (M-2, 14)
2aIII	160–162 (decomp.)	75	3.45 (4H, s), 7.23 (4H, m), 7.33 (2H, m), 7.52 (2H, m)	$C_{21}H_{12}O_2Cl_4$	1451s, 1380m, 1305m, 1290m, 1020s, 815s, 759s	442 (M+4, 3), 440 (M+2, 14), 442 (M, 23), 442 (M-2, 18)
2bII	223–225 (decomp.)	76	7.19 (2H, s), 7.45 (4H, m), 7.53 (2H, m), 7.94 (2H, m)	$C_{21}H_{10}O_2Br_4$	1440s, 1299m, 1279m, 1202m, 1020s, 957m, 774s	618 (M+4, 2), 616 (M+2, 13), 614 (M, 19), 612 (M-2, 13)
2bIII	203–205	86	7.19 (2H, s), 7.45 (4H, m), 7.53 (2H, m), 7.94 (2H, m)	$C_{21}H_{10}O_2Cl_4$	1460s, 1389m, 1310m, 1240m, 1029s, 820m, 800s	440 (M+4, 1), 438 (M+2, 11), 436 (M, 21), 434 (M-2, 16)

a Measured in $CDCl_3$ at 400 MHz. s, Singlet; m, multiplet.
b Satisfactory microanalyses were obtained: C, H ± 0.3.
c Obtained at 70 eV.

As a result, modification of the diarylmethylenephosphorane by binding two aryl groups is not enough to enhance generally the Wittig reactivity toward usual carbonyl compounds, albeit the 1,3-dioxole formed. In this respect, reactivity of **1a** and **1b** still resembles with that of diarylmethylenephosphorane. Semiempirical molecular orbital calculation[10] also showed that the optimized structure of **1a** resembles with that of diphenylmethylenetriphenylphosphorane as shown in FIGURE 1. To relieve the steric interference against the P-phenyl group, one of the two aryl groups was distorted and electrons of the highest occupied molecular orbital (HOMO) of **1a** delocalized chiefly in one of the aryl groups. On the other hand, in the optimized structure of **1b**, electrons did not delocalize on the diaryl moiety. These computational results show that the electronic structure of **1a** is similar to that of the diphenyl derivative, and the carbanion-electrons of **1b** are no longer delocalized even in one phenyl group. Although these tendencies are advantageous to elevate the Wittig reactivity, the electron density of the ylidic carbon is still insufficient as is suggested by calculated dipole moments of **1a** and **1b** which are 5.4 D and 5.2 D, respectively. Dipole moment of fluorenylidenetri-*n*-butylphosphorane, which is a reactivity enhanced version of the corresponding triphenylphosphorane, is 7.9 D[11] estimated by the same calculation. MOPAC calculations thus reasonably explain experimental results of **1**.

Moreover, in order to evaluate an ylidic character of **1a** and **1b**, it would be helpful to analyze chemical shifts of ^{31}P-NMR spectra by comparison with the reported data of analogous P-ylides.[12] In contrast to the proton NMR, in the expression of the shielding constant (σ) of the chemical shift (eq. 1), a local paramagnetic contribution (σ_p) is more important in heavy nuclei like ^{13}C and ^{31}P, etc. Especially in all contributions to σ_p in ^{13}C NMR (eq. 2[13]), the most important term is the $(r_i^{-3})_{2p_z}$, which is related to the charge density of a C-atom. Partial positive charge leads to a decrease in r_i (orbital contraction) and consequently to an increase in σ_p, and increased deshielding results. This charge-density dependence of ^{13}C-NMR chemical shifts is also applicable to those of ^{31}P NMR. Therefore, in the ylide-yllene resonance, the more the ylidic character contributes, the more positive chemical shift versus that of standard substance employed should be observed.

$$\sigma = \sigma_d + \sigma_p + \sigma' \qquad (1)$$

σ_d : local diamagnetic contribution
σ_p : local paramagnetic contribution
σ': effect of neighbouring group

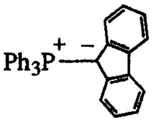
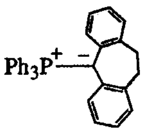
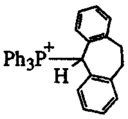
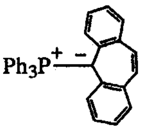
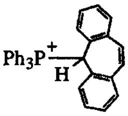
$$\sigma_p^i \approx -\frac{1}{\Delta E}\left(\frac{1}{r_i^3}\right)_{2p_z} \sum_{i \neq j} Q_{ij} \qquad (2)$$

ΔE: mean electronic excitation energy

r_i: the average radius of the carbon $2p_z$ orbitals

Q_{ij}: a bond order term

TABLE V ^{31}P-NMR Chemical shifts of some phosphorus ylides and the corresponding phosphonium salts

Phosphorus Ylide		*Phosphonium Salt*	
Compd	δ_{ppm}	*Compd*	δ_{ppm}
$Ph_3\overset{+}{P}-\overset{-}{C}(CN)_2$	27.2[a]	$Ph_3\overset{+}{P}-CH(CN)_2\ \overset{-}{Br}$	29.0[a]
$Ph_3\overset{+}{P}-\overset{-}{C}H_2$	20.3[a]	$Ph_3\overset{+}{P}-CH_3\ \overset{-}{Br}$	22.7[a]
$Ph_3\overset{+}{P}-\overset{-}{C}Me_2$	9.8[b]	$Ph_3\overset{+}{P}-CHMe_2\ \overset{-}{X}$	25.5[b]
$Ph_3\overset{+}{P}-\overset{-}{C}HPh$	7.1[a] 7.0[b]	$Ph_3\overset{+}{P}-CH_2Ph\ \overset{-}{Br}$ $Ph_3\overset{+}{P}-CH_2Ph\ \overset{-}{X}$	23.5 [a] 23.2[b]
	8.51[c]	---	---
 **1a**	10.91[d] 12.00[e]	 ClO_4^- **6aI**	--- 24.2[e]
 **1b**	10.36[d] 11.63[e]	 ClO_4^- **6bI**	--- 19.8[e]

[a] In $CDCl_3$. Literature data.[12a]; [b] In C_6D_6 at 28 °C. Literature data.[12b]; [c] In THF-d_8 at -20°C. [d] In THF-d_8 at 25 °C; [e] In DMSO-d_6 at 25 °C.

The data (TABLE V) showed clearly that ^{31}P-NMR chemical shifts of phosphonium salts appeared in almost a similar region irrespective of the solvent employed. By contrast, those of P-ylides were observed at the respective region reflecting the positive charge density on phosphorus. For example, although dicyanomethylenetriphenylphosphorane has a fair contribution of ylidic character, the same character of the dimethylmethylene derivative seems to be much lower. *A priori*, the fluorenylidene derivative is thus expected to have a similar nature of ylide-yllene resonance with that of dimethylmethylene and monophenylmethylene derivatives. Importantly, the objective ylides **1a** and **1b** do not have a large extent of the ylide-structure contribution. These data support lower reactivities of **1** in the usual Wittig reactivity with aldehydes and ketones. It is not, therefore, a promising idea to enhance the Wittig reactivity of stable diarylmethylenephosphoranes by etheno-bridging between two aryl groups.

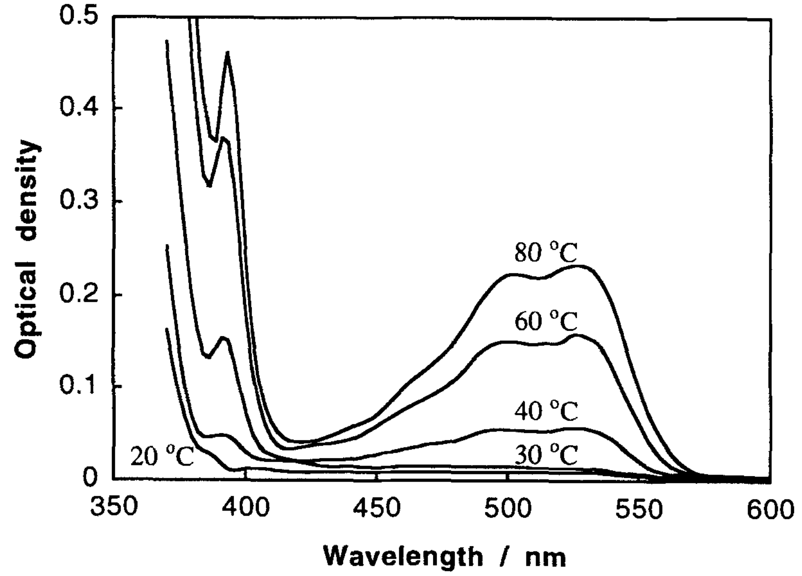
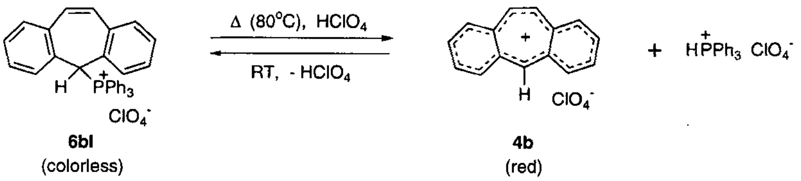


FIGURE 2 Temperature-dependent UV-VIS spectra of the salt **6bI** in MeCN. [**6bI**] = 0.14 M

On the purification stage of **6**, thermochromic behavior of its phosphonium salt **6bI** was observed in acetonitrile in the presence of trace perchloric acid. By contrast, **6aI** and **II** did not show any behavior under the same conditions. Temperature dependent UV-VIS spectra is shown in

FIGURE 2. The color change was observed when the spectrum was measured in acetonitrile but was faint in benzene and nitromethane, and the color remained unchanged in nitromethane on cooling again to room temperature. Furthermore, this thermochromism is also dependent on the kind of counteranion of the salt. That is, perchlorate is more suitable than bromide, and actually, **6bI** shows more intense red coloration at 80 °C and thermochromism lasts longer than that of **6bII.** Since no thermochromism of **6aI** and **II** was observed, conjugation of the two aromatic moieties seems to be crucial. Based on this conjecture and the temperature-dependent UV-VIS spectra (see, FIGURE 2 and the data of **1b** in TABLE II), the colored species was deduced not to be the ylide **1b**, but to be dibenzo[*a*,*e*]tropylium cation.[14] Authentic dibenzotropylium perchlorate, prepared by the literature procedure[14] from dibenzosuberol, substantiates the formation of such species.



Although nonpolar benzene does not stabilize the ionic species responsible for the thermochromic behavior of **6bI**, much polar nitromethane is suitable for stabilization for them. Hence, once coloration occurred at 80 °C, the color remained unchanged even upon cooling to room temperature in this solvent. On the counteranion effect, since bromide is more nucleophilic than perchlorate and gives **5b**, it does not exchange the free triphenylphosphine in the reversal process. As a result, this process corresponds to the reversal process of the preparation of the phosphonium salt **6bI** and appeared by the delicate balance between the solvent and counteranion properties.

EXPERIMENTAL

Melting points were determined in glass capillaries and are uncorrected. ^1H NMR spectra were recorded with Hitachi R-24B (60 MHz) or JEOL EX-400 (400 MHz), and ^{31}P NMR spectra were taken with JEOL

GSX-400 (162 MHz) spectrometers and chemical shifts were given in δ values. Tetramethylsilane was used as internal standard for ^1H NMR experiments and phosphoric acid (85% in H_2O) was used external standard for ^{31}P NMR experiments. IR and mass spectra were measured with Hitachi 260–10 and Shimadzu QP-1000 spectrometers, respectively. UV-VIS spectra were measured with Shimadzu UV-3000 spectrophotometer with a variable temperature accessory. Elemental analyses were performed with a Yanaco CHN corder model MT-5. Benzene is a suspect cocarcinogen and usual safety precaution is encouraged.

5-Bromodibenzosuberane (5a)

To dibenzosuberol (**3a**) (4.8 g, 22.8 mmol) was added acetyl bromide (12 mL, 148 mmol) and the mixture was immediately refluxed for 20 min. Then the resulting mixture was triturated with petroleum ether to give **5a** as colorless crystals (4.8 g, 18 mmol, yield 79%); mp 99–100 °C. ^1H NMR ($CDCl_3$) δ 3.06 (2H, dd-like, J=16, 10 Hz), 3.79 (2H, dd-like, J=16, 10 Hz), 6.41 (1H, s), 7.15–7.21 (4H, m), 7.24–7.29 (2H, m), 7.35–7.39 (2H, m). Anal. calcd. for $C_{15}H_{13}Br$: C, 65.95; H, 4.80%. Found: C, 65.89; H, 4.83%.

5-Bromodibenzosuberene (5b)

To dibenzosuberenol (**3b**) (14 g, 67 mmol) was added acetyl bromide (18 mL, 220 mmol) and the mixture was immediately refluxed for 30 min. After the excess acetyl bromide was removed *in vacuo*, the residue was recrystallized with ethyl acetate to give **5b** as light yellow needles (12.5 g, 46. mmol, yield 69%); mp 151–153 °C. (lit.[15]mp 118–120 °C). ^1H NMR ($CDCl_3$) δ 6.46 (1H, s), 7.10 (2H, s), 7.35 (8H, s). Anal. calcd. for $l_{15}H_{11}Br$: C, 66.44; H, 4.09%. Found: C, 66.60; H, 4.15%.

Dibenzosuberanyltriphenylphosphonium perchlorate (6aI)

To a methanolic solution (30 mL) of dibenzosuberol **3a** (5 g, 24 mmol), was added 10% perchloric acid (25 mL). Then, after addition of a nitromethane solution (20 mL) of triphenylphosphine (6.2 g, 24 mmol), the mixture was allowed to stand at 60 °C for 20 min. Cooling the solution gave the phosphonium salt **6aI** as colorless prisms (11 g, 20 mmol, yield 83%); mp 223–224 °C.

Dibenzosuberanyltriphenylphosphonium bromide (6aII)

A mixture of **5a** (1.0 g, 3.7 mmol) and triphenylphosphine (0.96 g, 3.7 mmol) was heated at 100 °C without solvent for 24 h. The resultant solid was recrystallized from ethanol-ether (1/4 volume ratio) to give **6aII** as colorless prisms (1.68g, 3.13.mmol, yield 86%); mp 207–210 °C.

Dibenzosuberenyltriphenylphosphonium perchlorate (6bI)

To a methanolic solution (50 mL) of dibenzosuberenol **3b** (4 g, 19 mmol), was added 10% perchloric acid (24 mL). Then, after addition of a nitromethane solution (20 mL) of triphenylphosphine (5.1 g, 19 mmol) to the methanolic solution, the mixture was allowed to stand at 60 °C for 20 min. Cooling the solution gave the phosphonium salt **6bI** as colorless prisms (8.8 g, 16 mmol, yield 83%); mp 233–234 °C.

Dibenzosuberenyltriphenylphosphonium bromide (6bII)

A dry benzene solution of **5b** (0.20 g, 0.74 mmol) and triphenylphosphine (0.20 g, 0.74 mmol) was refluxed for 1 h. The separated crystal was filtered and recrystallized from ethanol-ether (1/4 volume ratio) to give **6bII** as colorless prisms (0.34 g, 0.64 mmol, yield 86%); mp 219–220 °C.

Dibenzosuberanylidenetriphenylphosphorane (1a)

To the mixture of **6aI** (1.0 g, 1.8 mmol) and potassium *t*-butoxide (210 mg, 1.9 mmol) in the small reaction tube under N_2, was added a mixture of dry benzene (15 mL) and ether (15 mL) and stirred for 2 h. After a solid material was filtered in a dry box under N_2, the resulting red filtrate was concentrated *in vacuo* to give the orange **1a**. Recrystallization from dry benzene-petroleum ether gave pure **1a** as orange needles (677 mg, 1.49 mmol, yield 83%); mp 149–151 °C.

Dibenzosuberenylidenetriphenylphosphorane (1b)

To the mixture of **6bI** (1.0 g, 1.8 mmol) and potassium *t*-butoxide (210 mg, 1.9 mmol) in the small reaction tube under N_2, was added a mixture of dry benzene (15 mL) and ether (15 mL) and stirred for 2 h. After a solid material was filtered in a dry box under N_2, the resulting red solution was concentrated *in vacuo* to give the orange **1b**. Recrystallization from dry benzene-petroleum ether gave pure **1b** as red needles (600 mg, 1.33 mmol, yield 73%); mp 115–116 °C.

Reactions of Phosphoranes (1a *and* 1b) *with Tetrahalo o-quinones*

To a mixture of the phosphonium salt (**6aI** or **6bI**, *ca.* 500 mg, 0.9 mmol) and potassium *t*-butoxide (100 mg, 0.9 mmol) in a 20-mL Schlenk-type reaction tube, was added dry tetrahydrofuran (10 mL) under argon and cooling with an ice-salt bath. After the mixture was allowed to stand for 1 h with stirring magnetically, the resultant orange or red solution of an ylide was transferred to another small reaction vessel through G-3 glass filter to remove the separated $KClO_4$. To the filtrate, was added dropwise a tetrahydrofuran solution (5 mL) of tetrahalo *o*-quinone (0.6–0.8 mmol), the mixture was let stand for 0.5–1 h for completion of the reaction in an ice-salt bath, and then the solvent was removed *in vacuo* to give the crude 1,3-dioxole **2**. Recrystallization from ethanol gave pure colorless **2**.

Acknowledgements

This work was supported by Grant-in-Aid (09940691) for Scientific Research from the Ministry of Education, Science and Culture.

References

[1] A. Maercker, *Organic Reactions*, ed. by A. C. Cope (John Wiley & Sons, New York, 1965), Vol. 14, p. 272; G. W. Brown, R. C. Cookson and I. D. R. Stevens, *Tetrahedron Lett.*, 1263 (1964); W. W. Sullivan, D. Ullman and H. Shechter, *ibid.*, 457 (1969); A. Schönberg, E. Singer and H. Schulze-Pannier, *Chem. Ber.*, **106**, 2663 (1973); M. M. Sidky and L. S. Boulos, *Phosphorus, Sulfur and Silicon*, **19**, 27 (1984); K. Okuma, M. Shimasaki, K. Kojima, H. Ohta and R. Okazaki, *Chem. Lett.*, 1599 (1993).

[2] A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).

[3] Y. Kawamura, Y. Sato, T. Horie and M. Tsukayama, *Tetrahedron Lett.*, **38**, 7893 (1997); Y. Kawamura, T. Ohama and T. Horie, International Chemical Congress of Pasific Basin Societies, ORGN 535, December 17–22, Honolulu, USA, 1995.

[4] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919).

[5] L. A. Pinck and G. E. Hilbert, *J. Am. Chem. Soc.*, **69**, 723 (1947).

[6] L. Salisbury, *J. Org. Chem.*, **35**, 4258 (1970).

[7] E. D. Bergmann, G. Berthier, E. Fischer, Y. Hirshberg, D. Lavie, E. Loewenthal and B. Pullman, *Bull. Soc. Chim. Fr.*, 78 (1952).

[8] M. M. Sidky and L. S. Boulos, *Phosphorus, Sulfur and Silicon*, **19**, 27 (1984); Sidky, M. R. Mahran and L. S. Boulos, *ibid.*, **8**, 365 (1980); L.S. Boulos and M. M. Sidky, *Egypt. J. Chem.*, **26**, 547 (1983).

[9] H. J. Bestmann and H. J. Lang, *Tetrahedron Lett.*, 2101 (1969).

[10] Computer claculations were carried out using the CAChe-MOPAC program (Release 6.1) available from Sony-Tektronix, Co. Semiempirical PM3 SCF-MO calculations were executed: J. J. P. Stewart, *J. Comput. Chem.*, **10**, 221 (1989).

[11] The dipole moment of fluorenylidenetriphenyl derivative measured in benzene at 25°C, was reported as 7.09 D: A. W. Johnson, *J. Org. Chem.*, **24**, 282 (1959).

[12] (a) P. J. Butterfield, J. C. Tebby and T. J. King, *J. Chem. Soc., Perkin 1*, 1237 (1978); (b) T. A. Albright, M. D. Gordon, W. J. Freeman and E. E. Schweizer, *J. Am. Chem. Soc.*, **98**, 6249 (1976).

[13] H. Günther, *NMR Spectroscopy*, (John Wiley & Sons, Chichester, 1994), 2nd ed., Chap. 11, pp. 494–501.

[14] G. Berti, *J. Org. Chem.*, **22**, 230 (1957).

[15] G. Bellucci, C. Chiappe, F. Marioni, and F. Marchetti, *J. Phys. Org. Chem.*, **4**, 387 (1991): Melting point was apparently different from our data. Published data seemed to be the data of the precursor, 5-dibenzosuberenol (mp 119 °C).