General Synthesis of Phosphonates from Heteroniaanthracene Cations and Their Use in Wittig-Horner Reaction

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Heteroaromatic cations such as 9-heteroniaanthracene (acridinium, xanthylium, and thioxanthylium) and 1-thionianaphthalene (thiochromenylium) ions reacted with trimethyl phosphite in the presence of sodium iodide in acetonitrile at room temperature to give the corresponding phosphonates (**2** and **4**) respectively in 76—92% yields. The phosphonates were deprotonated with butyllithium in THF at −78 °C, and the resulting carbanions reacted with *p*-tolualdehyde, cinnamaldehyde, and 4,4′-dichlorobenzophenone to afford the corresponding exomethylene containing heterocyclic compounds, respectively, in 52—96% yields. However, the phosphonate carbanions derived from **2** did not react with cycloalkanones and butanal.

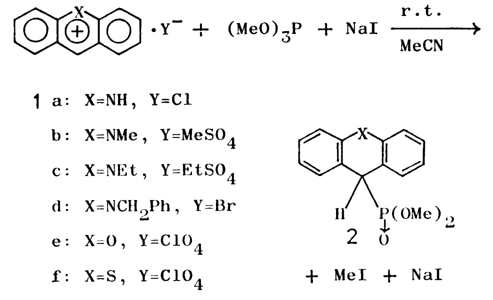
The reactions of heteroaromatic cations with a wide variety of nucleophiles have been investigated extensively. However, there are only a few reports on the reactions with phosphorus nucleophiles such as phosphines and phosphites.[1)] Evenmore, the utilization of the expected reaction products (*e.g.*, phosphonium salts or phosphonates) as reagents for carbonyl olefination has been described only by two reports, one on the use of the phosphonium salt obtained from pyrylium perchlorate[1a)], and the other on that of phosphonates obtained from acridinium salts.[1f)]

The preceding paper and its preliminary reports showed that 1,3-dithiolylium salts reacted with phosphines or phosphites to give the corresponding phosphonium salts or phosphonates in high yields and that they, especially the latter, could be used in Wittig-Horner reaction to give various derivatives of 1,4-dithiafulvenes and fulvalenes in high yields.[2)] Consequently, versatile utility in the synthesis of heterocyclic compounds was expected for analogous phosphonates, if they could be prepared from heteroaromatic cations and trialkyl phosphite.

We report here a general synthesis of the phosphonates[3)] from heteroaromatic cations such as acridinium, xanthylium, thioxanthylium, and thiochromenylium ions, and their use in Wittig-Horner reaction.

Results and Discussion

Preparation of Phosphonates from Heteroaromatic Cations. Under a nitrogen atmosphere at room temperature, trimethyl phosphite was added at once to a stirred solution of 9-heteroniaanthracene salt (acridinium, xanthylium, or thioxanthylium salts) (**1a**—**f**) in dry acetonitrile, then immediately sodium iodide was added, and the solution was stirred for 1 h. Usual treatment of the mixture gave the corresponding phosphonate (**2a**—**f**) in high yields. The results are shown in Table 1.



1 a: X=NH, Y=Cl
b: X=NMe, Y=$MeSO_4$
c: X=NEt, Y=$EtSO_4$
d: X=NCH_2Ph, Y=Br
e: X=O, Y=ClO_4
f: X=S, Y=ClO_4

Scheme 1.

Table 1. Yields, mp, and IR spectral data of the phosphonates (**2**)

Compound	Yield (%)	Mp (°C)	IR (KBr) (cm^{-1}) $\nu_{P=O}$	ν_{P-O-C}	
2a	85	170.0—171.0	1225	1055(as)	1030(s)
2b	85	98.0—99.0	1270 or 1240	1045(as)	1020(s)
2c	92	100.0—100.5	1260 or 1250	1060(as)	1020(s)
2d	76	147.0—148.0	1240	1060(as)	1030(s)
2e	90	132.0—133.0	1255	1050(as)	1020(s)
2f	87	194.0—195.0	1245	1055(as)	1025(s)

The structure of **2a**—**f** was confirmed by means of elemental analyses, IR, ^{1}H-NMR, and mass spectra.

As shown in Table 1, the IR spectra of **2a**—**f** showed strong absorption bands at 1225—1270 (P=O), 1045—1060, and 1020—1030 cm^{-1} (P-O-C). The IR spectrum of **2a** showed also a sharp absroption band at 3270 cm^{-1} (NH).

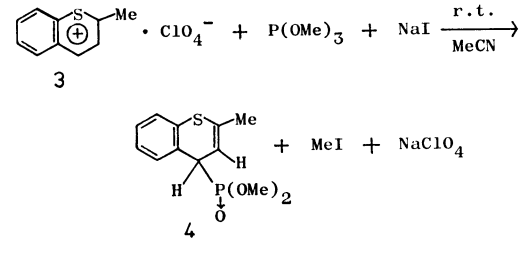
All **2a**—**f** gave reasonable ^{1}H-NMR spectra, each of which showed a doublet signal at δ 3.46—3.53 due to $POCH_3$ (J_{POCH}=10.5 Hz), and a doublet signal at δ 4.49—4.69 with a relatively large value of coupling constnat (J=24.8—28.7 Hz) assignable to PCH. This fact will be discussed later.

The ^{31}P-NMR spectrum of **2e** exhibited a signal at δ_P −24 ppm supporting the phosphonate structure.[4)]

The mass spectra of the phosphonates (**2a**—**f**) showed the parent peak (3—6%), the base peak assignable to M$^+$−P(O)(OMe)$_2$, and the metastable peak due to the direct fragmentation of the parent ion to the M$^+$−P(O)(OMe)$_2$ ion.

As described above, it was ascertained first that the Michaelis-Arbuzov reaction of 9-heteroniaanthracene salt (**1a**—**f**) with trimethyl phosphite proceeded easily even at room temperature in the presence of sodium iodide in acetonitrile, similarly to the case of 1,3-dithiolylium salt.[2)]

Furthermore, 2-methyl-1-thionianaphthalene perchlorate [(2-methyl)thiochromenylium perchlorate] (**3**) was also allowed to react with trimethyl phosphite under the same conditions to give 4-dimethoxyphosphinyl-2-methyl-4*H*-1-thianaphthalene (**4**; yield 91%) exclusively.



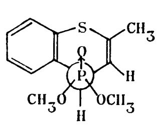
Scheme 2.

The structure of **4** was confirmed by means of elemental analysis, IR, ^{1}H-NMR, and mass spectra, and was also supported by the result of its reaction with 4,4′-dichlorobenzophenone described later. The isomeric structure, 2-dimethoxyphosphinyl-2-methyl-2*H*-1-thianaphthalene was ruled out based on the ^{1}H-NMR spectral data.

The IR spectrum of **4** showed strong absorptions at 1240 (P=O), 1055, and 1025 cm^{-1} (P–O–C).

The phosphonate (**4**) exhibits a rather complex ^{1}H-NMR spectrum compared with those of **2** due to the presence of an asymmetric carbon atom at the 4-position, however, it is fully assigned as shown in Table 2.

Table 2. ^{1}H-NMR spectral data of the phosphonate (**4**) (in $CDCl_3$)

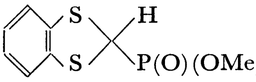
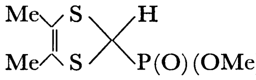
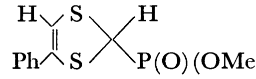
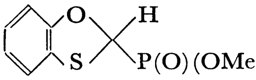
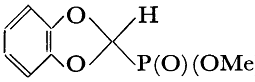
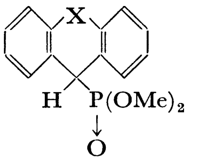
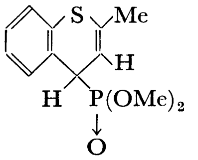
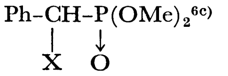
	δ 2.06 (3H, ddd, $J_{PCCCCH}=6.0$, $J_{HCCCH}=1.4$, $J_{HCCCCH}=0.9$ Hz, 2-C-CH_3);
	3.61 (3H, d, $J_{POCH}=10.4$ Hz, $POCH_3$);
	3.72 (3H, d, $J_{POCH}=10.4$ Hz, $POCH_3$);
	4.18 (1H, qdd, $J_{PCH}=28.5$, $J_{HCCH}=6.8$, $J_{HCCCCH}=0.9$ Hz, 4-CH);
	5.62 (1H, qdd, $J_{HCCH}=6.8$, $J_{PCCH}=4.2$, $J_{HCCCH}=1.4$ Hz, 3-CH);
	7.18 (4H, br s, aromatic H)

There are two significant features in relation to the coupling constants between phosphorus and hydrogen: (a) the J_{PCH} value (28.5 Hz) is one of the largest ones ever known and is much larger than J_{PCCH} (4.2 Hz), usually the reverse should be the case,[5] and (b) the long range coupling between phosphorus and 2-C–CH_3 ($J_{PCCCH}=6.0$ Hz) is exceptionally large. These facts were confirmed by comparison of the spectra obtained at 60 MHz and at 100 MHz. Moreover, the 2-C–CH_3 signal was irradiated to give double doublet signals for 3-CH and 4-CH with the coupling constants shown above.

The mass spectrum of **4** showed the parent peak at *m/e* 270 (5%), the base peak at *m/e* 161 assignable to $M^+-P(O)(OMe)_2$, and the metastable peak at *m/e* 96.0 due to the direct fragmentation of the parent ion to the $M^+-P(O)(OMe)_2$ ion.

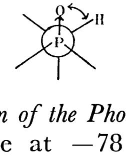
Chemical shifts and coupling constants of PCH of related phosphonates are shown in Table 3. These facts can be summarized as follows: i) coupling constants (J_{PCH}) of phosphonates of 1,3-dithioles lie around 5 Hz, these of 1,3-oxathioles around 8 Hz, those of 1,3-dioxoles around 30 Hz, and those of 1-hetera-2,5-cyclohexadienes around 27 Hz and ii) an electronegative group increases the coupling constants.

Table 3. Chemical shifts and coupling constants of PCH of related phosphonates (in $CDCl_3$)

Compound		PCH (δ)	J_{PCH} (Hz)
		4.75	5.8
		4.73	4.5
		5.06	4.5
 [6a,b)]		6.08	8.2
 [6a,b)]		6.22	29.8
	X=NH	4.58	24.9
	X=NMe	4.55	26.1
	X=O	4.49	24.8
	X=S	4.69	28.7
		4.18	28.5
 $\underset{X}{Ph\text{-}CH}\text{-}\underset{O}{\overset{}{P}}(OMe)_2$[6c)]	X=Cl	4.97	14.0
	X=OAc	6.13	13.5
	X=OTs	5.62	15.5

a) In CCl_4.

Costisella and Gross suggested recently that there is a relationship similar to Karplus equation between the value of J_{PCH} and the dihedral angle (β) for phosphinyl-containing compounds.[6b)] However, bond lengths (C–H and C–P) and bond angle (∠HCP) should also be important factors and detailed discussion cannot be given here.



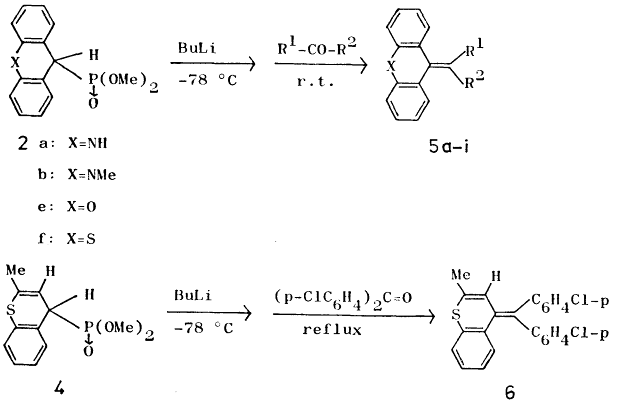
Wittig-Horner Reaction of the Phosphonates. Under a nitrogen atmosphere at −78 °C, butyllithium in hexane was added to stirred solution of the phosphonate (**2a**, **b**, **e**, or **f**) in tetrahydrofuran (THF). The resulting carbanion was allowed to react with a carbonyl compound to give the exo-methylene-containing compound (**5**) in a high yield. The reaction with *p*-tolu-

Table 4. Yields and mp of **5** and **6**

Product	X	R^1	R^2	Yield (%)	Mp (°C)
5a[a]	NH	p-$CH_3C_6H_4$	H	53	164.0—166.0 (dec)
5b	NMe	p-$CH_3C_6H_4$	H	93	127.5—128.5
5c	O	p-$CH_3C_6H_4$	H	84	112.0—113.0
5d	S	p-$CH_3C_6H_4$	H	93	128.0—129.0
5e	NMe	PhCH=CH	H	96	112.5—113.5
5f	O	PhCH=CH	H	91	91.0— 92.0
5g	S	PhCH=CH	H	92	165.0—166.0
5h	NMe	p-ClC_6H_4	p-ClC_6H_4	52	257.0—258.0
5i	O	p-ClC_6H_4	p-ClC_6H_4	95	209.0—210.0
5j	S	p-ClC_6H_4	p-ClC_6H_4	—	—
6		p-ClC_6H_4	p-ClC_6H_4	78	158.5—159.5

a) See the text.

aldehyde and cinnamaldehyde took place rapidly at low temperature (−78 °C to room temperature) but that with 4,4′-dichlorobenzophenone was effected in refluxing THF. The phosphonate (**4**) was also deprotonated and the resulting carbanion reacted with 4,4′-dichlorobenzophenone to give 4-[bis(p-chlorophenyl)methylene]-2-methyl(thiochromene) (**6**). The reaction of **2f** and 4,4′-dichlorobenzophenone did not proceed even under reflux, and the starting materials were recovered (**2f**; 58%; ketone, 73%).[7] The results are shown in Table 4.



Scheme 3.

The structures of **5** and **6** were confirmed by means of elemental analyses, IR, ^{1}H-NMR, and MS. The molecular ion peak is in each case the most intense peak in the mass spectra except for **5e** (M$^+$, 63%; M$^+$−Ph, 100%). The structure of **5a** was confirmed to be 9-(p-methylbenzyl)acridine formed by prototropy of the initially produced benzylidene type compound (absence of NH in IR and presence of a methylene group in NMR).

Furthermore, the reaction of the phosphonate carbanion derived from **2b** or **2e** with cycloalkanones (*e.g.*, cyclohexanone or cyclopentanone) and butanal was tried, however, the expected product could not be obtained even under reflux and the starting material (**2b** or **2e**) was recovered exclusively. The inertness of the reaction seems to be attributable chiefly to steric hindrance between the peri-hydrogens of the phosphonate (**2**) and the α-methylene hydrogens of a carbonyl compound.

Experimental

All the melting points are not corrected. IR spectra were measured with a Hitachi EPI-G2 spectrometer, ^{1}H-NMR spectra with Hitachi R-20B, Hitachi R-24 (60 MHz), and JEOL JNM-4H-100 (100 MHz) spectrometers (TMS as an internal standard), and MS with a Hitachi RMU-6L mass spectrometer at 70 eV. ^{31}P-NMR spectra were measured with a Hitachi R-20B-R-204-PB (24.3 MHz) spectrometer using 85% phosphoric acid as an external standard.

Materials: *9-Azoniaanthracene Salts (Acridinium Salts) (**1a—d**).* Each 9-azoniaanthracene salt was prepared by the reaction of 9-azaanthracene (aciridine) with RX in good yields.

Compound	R	X	Mp (°C)
1a	H	Cl	220.5—222 (dec)[1c],[a]
1b	Me	$MeSO_4$	207—208 (dec)[8],[a]
1c	Et	$EtSO_4$	275—277 (dec)[8],[a]
1d	$PhCH_2$	Br	225—227 (dec) [lit,[9] 209 (dec)]

a) Melting points were not indicated for **1a**, **1b**, and **1c** in the literatures.

9-Oxoniaanthracene perchlorate (xanthylium perchlorate) (**1e**) was prepared by the treatment of 10H-9-oxaanthracen-10-ol (mp 125—126 °C, lit,[10] 124—126 °C), which was obtained by the reduction of xanthone (5.89 g, 0.03 mol) with sodium borohydride (2.3 g) in refluxing absolute methanol (150 ml), with 70% perchloric acid (20 ml) in dry ether (200 ml) at −78 °C, mp 237 °C (dec) (lit,[11] mp 225—226 °C), total yield 7.40 g (88%).

9-Thioniaanthracene perchlorate (thioxanthylium perchlorate) (**1f**) was prepared from thioxanthone (6.4 g, 0.03 mol) by the same procedure as **1e** in total ylied of 6.14 g (69%), mp 229—230 °C (dec) (lit, mp 217—219 °C[12], 229 °C[13]).

2-Methyl-1-thionianaphthalene perchlorate (**3**) was prepared from 2-methyl-4H-1-thianaphthalen-4-one[14] (5.28 g, 0.03 mol) by the same procedure as **1e** in total yield of 5.70 g (73%), mp 143—145 °C. This compound was colored blue due to the presence of a small amount of impurity (*e.g.*, cyanine dye) but was used for the next step without further purification because of its instability.

Michaelis-Arbuzov Reaction of Heteroaromatic Cations with Trimethyl Phosphite. *General Procedure*: Trimethyl phosphite (1.2 ml, 10 mmol) was added to a stirred solution of heteroaromatic cation (10 mmol) in dry acetonitrile (50 ml) at room temperature under nitrogen and then followed with dry sodium iodide (1.5 g, 10 mmol). After the mixture had been stirred for 1 h, the solvent was evaporated under reduced pressure. Water (50 ml) was added to the residue and the product was extracted with dichloromethane (30 ml × 3). The combined extracts were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Recrystallization of the residue from ethyl acetate and ether gave the corresponding phosphonate. Dry column chromatography (neutral alumina) was often used for purification.

Reaction of 9-azoniaanthracene chloride (**1a**) with trimethyl phosphite gave 10-dimethoxyphosphinyl-9,10-dihydro-9-azaanthracene (**2a**), yield 85%, mp 170.0—171.0 °C (from AcOEt); IR (KBr): 3270 (NH), 1480, 1225 (P=O), 1055, and 1030 cm^{-1} (P–O–C); ^{1}H-NMR ($CDCl_3$): δ 3.53 (d, $J_{\mathrm{POCH}}=10.5$ Hz, 6H, $POCH_3$), 4.58 (d, $J_{\mathrm{PCH}}=24.9$ Hz, 1H, PCH), and 6.5—7.4 (m, 9H, aromatic and NH); MS: *m/e* 289 (M^+, 4%), 180 ($M^+-P(O)(OMe)_2$, 100), 179 (180 −H, 15), and 152 (180−CH_2N, 5); metastable ion, found: 112.1 calcd for 289→180: 112.1; found: 128.4, calcd for 180→152: 128.36.

Found: C, 62.19; H, 5.66; N, 4.62%. Calcd for $C_{15}H_{16}NO_3P$: C, 62.28; H, 5.58; N, 4.84%.

Reaction of 9-methyl-9-azoniaanthracene methyl sulfate (**1b**) with trimethyl phosphite gave 10-dimethoxyphosphinyl-9-methyl-9,10-dihydro-9-azaanthracene (**2b**), yield 85%, mp 98.0—99.0 °C (from AcOEt and Et_2O); IR (KBr): 1580, 1470, 1240 (P=O), 1045, and 1020 cm^{-1} (P–O–C); ^{1}H-NMR ($CDCl_3$): δ 3.39 (s, 3H, NCH_3), 3.49 (d, $J_{\mathrm{POCH}}=10.5$ Hz, 6H, $POCH_3$), 4.55 (d, $J_{\mathrm{PCH}}=26.1$ Hz, 1H, PCH), and 6.7—7.5 (m, 8H, aromatic); MS: *m/e* 303 (M^+, 6%), 194 ($M^+-P(O)(OMe)_2$, 100), and 179 (194−Me, 17); metastable ion, found: 124.2, calcd for 303→194: 124.21; found: 165.2, calcd for 194→179: 165.16.

Found: C, 63.11; H, 6.05; N, 4.53%. Calcd for $C_{16}H_{18}NO_3P$: C, 63.36; H, 5.98; N, 4.62%.

Reaction of 9-ethyl-9-azoniaanthracene ethyl sulfate (**1c**) with trimethyl phosphite gave 10-dimethoxyphosphinyl-9-ethyl-9,10-dihydro-9-azaanthracene (**2c**), yield 92%, mp 100.0—100.5 °C (from PhH and CH_2Cl_2); IR (KBr): 1590, 1260 or 1250 (P=O), 1060, and 1020 cm^{-1} (P–O–C); ^{1}H-NMR ($CDCl_3$): δ 1.38 (t, $J=6.8$ Hz, 3H, N-C-CH_3), 3.46 (d, $J_{\mathrm{POCH}}=10.5$ Hz, 6H, $POCH_3$), 3.99 (q, $J=6.8$ Hz, 2H, N-CH_2-C), 4.52 (d, $J_{\mathrm{PCH}}=25.5$ Hz, 1H, PCH), and 6.7—7.5 (m, 8H, aromatic); MS: *m/e* 317 (M^+, 6%), 208 (M^+-P(O) $(OMe)_2$, 100), 180 (208−C_2H_4, 22), and 152 (180−CH_2N, 4); metastable ion, found: 136.5, calcd for 317→208: 136.48; found 155.8, calcd for 208→180: 155.77; found 128.4, calcd for 180→152: 128.36.

Found: C, 64.16; H, 6.44; N, 4.57%. Calcd for $C_{17}H_{20}NO_3P$: C, 64.35; H, 6.35; N, 4.41%.

Reaction of 9-benzyl-9-azoniaanthracene bromide (**1d**) with trimethyl phosphite gave 9-benzyl-10-dimethoxyphosphinyl-9,10-dihydro-9-azaanthracene (**2d**), yield 76%, mp 147.0—148.0 °C (from AcOEt); IR (KBr): 1470, 1240 (P=O), 1060, and 1030 cm^{-1} (P–O–C); ^{1}H-NMR ($CDCl_3$): δ 3.52 (d, $J_{\mathrm{POCH}}=10.5$ Hz, 6H, $POCH_3$), 4.62 (d, $J_{\mathrm{PCH}}=25.7$ Hz, 1H, PCH), 5.18 (s, 2H, N-CH_2-Ph), and 6.5—7.5 (m, 13H, aromatic); MS: *m/e* 379 (M^+, 6%), 270 ($M^+-P(O)(OMe)_2$, 100), and 179 (270−$PhCH_2$, 19); metastable ion, found: 192.4, calcd for 379→270: 192.35.

Found: C, 69.58; H, 5.98; N, 3.51%. Calcd for $C_{22}H_{22}NO_3P$: C, 69.65; H, 5.85; N, 3.69%.

Reaction of 9-oxoniaanthracene perchlorate (**1e**) with trimethyl phosphite gave 10-dimethoxyphosphinyl-10*H*-9-oxaanthracene(**2e**), yield 90%, mp 132.0—133.0 °C (from AcOEt and Et_2O) (lit,[15] 128—129 °C); IR (KBr): 1475, 1255 (P=O), 1050, and 1020 cm^{-1} (P–O–C); ^{1}H-NMR ($CDCl_3$): δ 3.53 (d, $J_{\mathrm{POCH}}=10.5$ Hz, 6H, $POCH_3$), 4.49 (d, $J_{\mathrm{PCH}}=24.8$ Hz, 1H, PCH), and 6.9—7.5 (m, 8H, aromatic): ^{31}PNMR ($CDCl_3$): $\delta_{\mathrm{P}}-24$ ppm; MS: *m/e* 290 (M^+, 3%), and 181 ($M^+-P(O)(OMe)_2$, 100).

Reaction of 9-thioniaanthracene perchlorate (**1f**) with trimethyl phosphite gave 10-dimethoxyphosphinyl-10*H*-9-thiaanthracene (**2f**), yield 87%, mp 194.0—195.0 °C (from AcOEt and Et_2O); IR (KBr): 1245 (P=O), 1055 and 1025 cm^{-1} (P–O–C); ^{1}H-NMR ($CDCl_3$): δ 3.52 (d, $J_{\mathrm{POCH}}=10.5$ Hz, 6H, $POCH_3$), 4.69 (d, $J_{\mathrm{PCH}}=28.7$ Hz, 1H, PCH), and 7.1—7.5 (m, 8H, aromatic); MS: *m/e* 306 (M^+, 5%) and 197 ($M^+-P(O)(OMe)_2$, 100).

Found: C, 58.63; H, 5.06; S, 10.55%. Calcd for $C_{15}H_{15}O_3PS$: C, 58.82; H, 4.94; S, 10.47%.

Reaction of 2-methyl-1-thionianaphthalene perchlorate (**3**) with trimethyl phosphite gave 4-dimethoxyphosphinyl-2-methyl-4*H*-1-thianaphthalene (**4**), yield 91%, mp 99.0—100.0 °C (from AcOEt); IR (KBr): 1240 (P=O), 1055, and 1025 cm^{-1} (P–O–C); ^{1}H-NMR ($CDCl_3$): δ 2.06 (ddd, $J_{\mathrm{PCCCCH}}=6$, $J_{\mathrm{HCCCH}}=1.4$, $J_{\mathrm{HCCCCH}}=0.9$ Hz, 3H, 2-C-CH_3), 3.61 (d, $J_{\mathrm{POCH}}=10.4$ Hz, 3H, $POCH_3$), 3.72 (d, $J_{\mathrm{POCH}}=10.4$ Hz, 3H, $POCH_3$), 4.18 (qdd, $J_{\mathrm{PCH}}=28.5$, $J_{\mathrm{HCCH}}=6.8$, $J_{\mathrm{HCCCH}}=0.9$ Hz, 1H, 4-CH), 5.62 (qdd, $J_{\mathrm{HCCH}}=6.8$, $J_{\mathrm{PCCH}}=4.2$, $J_{\mathrm{HCCCH}}=1.4$ Hz, 1H, 3-CH), and 7.18 (br s, 4H, aromatic); (100 MHz, in $CDCl_3$): δ 2.06 (ddd, 3H, 2-C-CH_3), 3.61 (d, 3H, $POCH_3$), 3.72 (d, 3H, $POCH_3$), 4.18 (qdd, 1H, 4-CH), 5.62 (qdd, 1H, 3-CH), and 7.18 (br s, 4H, aromatic). The 2-C-CH_3 signal at δ 2.06 was irradiated to give double doublet signals for 3-CH (δ 5.62) and 4-CH (δ 4.18) with the coupling constants shown above.

MS: *m/e* 270 (M^+, 5%), 161 ($M^+-P(O)(OMe)_2$, 100), 128 (161−SH, 10), and 155 (161−CH_2S, 6); metastable ion, found: 96.0, calcd for 270→161: 96.0; found 101.8, calcd for 161→128: 101.76.

Found: C, 53.17; H, 5.84; S, 11.37%. Calcd for $C_{12}H_{15}O_3PS$: C, 53.33; H, 5.59; S, 11.86%.

Witting-Horner Reaction of the Phosphonates Derived from Heteroaromatic Cations. *General Procedure*: To a stirred solution of a phosphonate (1.0 mmol) in THF (10 ml), butyllithium in hexane (0.75 ml, 1.15 mmol) was added at −78 °C under nitrogen. The solution colored yellow or yellowish brown due to the resulting carbanion. After 10 min, a solution of a carbonyl compound (1.0 mmol) in THF (5—10 ml) was added. Stirring was continued for 10 min at −78 °C and the mixture was then allowed to get warm to room temperature. When the carbonyl compound was not an aldehyde but a ketone, the reaction mixture was heated under reflux for 30 min. The solvent was evaporated under reduced pressure and the mixture was extracted with dichloromethane (20 ml × 3) after addition of water (50 ml). The combined extracts were dried over anhydrous magnesium sulfate, the solvent was evaporated, and the residue was recrystallized to give the corresponding product.

Reaction of **2a** with *p*-tolualdehyde gave 9-(*p*-methylbenzyl) acridine (**5a**), yield 53%, mp 164.0—166.0 °C (dec) (from MeOH); IR (KBr): 1510, 770, 760, and 740 cm^{-1}; ^{1}H-NMR (CCl_4): δ 2.24 (s, 3H, CH_3), 4.89 (s, 2H, CH_2), 6.95 (s, 4H, aromatic), and 7.1—8.4 (m, 8H, aromatic); MS: *m/e* 283 (M^+, 100%), 282 (M^+-H, 49), 268 (M^+-Me, 50), 267 (268−H, 38), 141 (282^{2+}, 15), and 134 (268^{2+}, 31).

Found: C, 89.02; H, 5.85; N, 5.09%. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94%.

Reaction of **2b** with *p*-tolualdehyde gave 10-methyl-9-(*p*-tolylmethylene)-9,10-dihydroacridine (**5b**), yield 93%, mp 127.5—128.5 °C (from MeOH); IR (KBr): 1580, 1445, 860, 815, and 755 cm^{-1}; ^{1}H-NMR (CCl_4): δ 2.32 (s, 3H, Ar-CH_3), 3.48 (s, 3H, N-CH_3), and 6.4—7.7 (m, 13H, aromatic and olefinic); MS: *m/e* 297 (M^+, 100%), 296 (M^+−H, 51), 282 (M^+−Me, 16), 281 (296−Me, 25), 267 (282−Me, 19), 266 (281−Me, 23), 148.5 (M^{2+}, 11), 141 (282^{2+}, 22), and 140.5 (281^{2+}, 35).

Found: C, 88.60; H, 6.29; N, 5.00%. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71%.

Reaction of **2e** with *p*-tolualdehyde gave 9-(*p*-tolylmethylene) xanthene (**5c**), yield 84%, mp 112.0—113.0 °C (from MeOH); IR (KBr): 1440, 1250, 805, 760, and 745 cm^{-1}; ^{1}H-NMR (CCl_4): δ 2.33 (s, 3H, CH_3) and 6.5—7.8 (m, 13H, aromatic and olefinic); MS: *m/e* 284 (M^+, 100%), 283 (M^+−H, 24), 269 (M^+−Me, 36), 268 (283−Me, 56), 142 (M^{2+}, 8), 134.5 (269^{2+}, 13), and 134 (268^{2+}, 30).

Found: C, 88.44; H, 5.54%. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67%.

Reaction of **2f** with *p*-tolualdehyde gave 9-(*p*-tolylmethylene) thioxanthene (**5d**), yield 93%, mp 128.0—129.0 °C (from MeOH); IR (KBr): 1430, 815, 770, 760, and 740 cm^{-1}; ^{1}H-NMR (CCl_4): δ 2.30 (s, 3H, CH_3) and 6.5—7.8 (m, 13H, aromatic and olefinic); MS: *m/e* 300 (M^+, 100%), 285 (M^+−Me, 46), 284 (285−H, 49), 252 (285−SH, 22) and 142 (284^{2+}, 38).

Found: C, 84.20; H, 5.20; S, 10.68%. Calcd for $C_{21}H_{16}S$: C, 83.96; H, 5.37; S, 10.67%.

Reaction of **2b** with *trans*-3-phenyl-2-propenal gave 10-methyl-9-(3-phenyl-2-propenylidene)-9,10-dihydroacridine (**5e**), yield 96%, mp 112.5—113.5 °C (from EtOH); IR (KBr): 1580, 1450, 760, and 745 cm^{-1}; ^{1}H-NMR (CCl_4): δ 3.37 (s, 3H, N-CH_3) and 6.2—7.7 (m, 16H, aromatic and olefinic); MS: *m/e* 309 (M^+, 63%), 308 (M^+−H, 46), 232 (M^+−Ph, 100).

Found: C, 89.24; H, 6.09; N, 4.42%. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53%.

Reaction of **2e** with *trans*-3-phenyl-2-propenal gave 9-(3-phenyl-2-propenylidene)xanthene (**5f**), yield 91%, mp 91.0—92.0 °C (from EtOH); IR (KBr): 1595, 1450, 1310, 1270, 945, 770, 765, 750, and 695 cm^{-1}; ^{1}H-NMR (CCl_4): δ 6.4—7.8 (m, aromatic and olefinic); MS: *m/e* 296 (M^+, 100%), 295 (M^+−H, 86), 219 (M^+−Ph, 97), and 218 (296−Ph, 46).

Found: C, 89.02; H, 5.21%. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44%.

Reaction of **2f** with *trans*-3-phenyl-2-propenal gave 9-(3-phenyl-2-propenylidene)thioxanthene (**5g**), yield 92%, mp 165.0—166.0 °C (from EtOH); IR (KBr): 1455, 1430, 970, 765, 740, and 690 cm^{-1}; ^{1}H-NMR (CCl_4): δ 6.4—7.8 (m, aromatic and olefinic); MS: *m/e* 312 (M^+, 100%), 311 (M^+−H, 68), 235 (M^+−Ph, 78), 234 (311−Ph, 40), 221 (235−CH_2, 26), and 202 (235−SH, 11).

Found: C, 84.85; H, 5.00; S, 10.22%. Calcd for $C_{22}H_{16}S$: C, 84.58; H, 5.16; S, 10.26%.

Reaction of **2b** with 4,4′-dichlorobenzophenone gave 10-methyl-9-[bis(*p*-chlorophenyl)methylene]-9,10-dihydroacridine (**5h**), yield 52%, mp 257.0—258.0 °C (from EtOH); IR (KBr): 1590, 1455, 1350, 1095, 820, 810, and 755 cm^{-1}; ^{1}H-NMR (CCl_4 and $CDCl_3$, 1:1): δ 3.50 (s, 3H, N-CH_3) and 6.4—7.5 (m, 16H, aromatic); MS: *m/e* 431 (M^+ for two ^{37}Cl, 12%), 430 (25), 429 (M^+ for one ^{37}Cl and one ^{35}Cl, 80), 428 (44), and 427 (M^+ for two ^{35}Cl, 100).

Found: C, 75.95; H, 4.48; N, 3.32; Cl, 16.98%. Calcd for $C_{27}H_{19}NCl_2$: C, 75.71; H, 4.47; N, 3.27; Cl, 16.55%.

Reaction of **2e** with 4,4′-dichlorobenzophenone gave 9-[bis(*p*-chlorophenyl)methylene]xanthene (**5i**), yield 95%, mp 209.0—210.0 °C (from MeOH); IR (KBr): 1440, 1250, 1090, 1015, 825, 760, and 755 cm^{-1}; MS: *m/e* 418 (M^+ for two ^{37}Cl, 14%), 417 (20), 416 (M^+ for one ^{37}Cl and one ^{35}Cl, 68), 415 (32), 414 (M^+ for two ^{35}Cl, 100), 378 (M^+−HCl, 28), and 342 (378−HCl, 17).

Found: C, 75.49; H, 3.63; Cl, 16.95%. Calcd for $C_{26}H_{16}OCl_2$: C, 75.19; H, 3.88; Cl, 17.07%.

Reaction of **2f** with 4,4′-dichlorobenzophenone gave no expected product and the starting materials (4,4′-dichlorobenzophenone, 73%, and **2f**, 58%) were recovered. Moreover, 10*H*-9-thiaanthracen-10-one was detected by thin-layer chromatography (SiO_2/CH_2Cl_2).

Reaction of **2b** or **2e** with cycloalkanones (*e.g.*, cyclohexanone and cyclopentanone) did not take place under general procedure and the color of the carbanion (**2b**, brown; **2e**, orange) disappeared, when the solution was refluxed. However, the expected product could not be obtained and the starting material (**2b** or **2e**) was recovered.

Reaction of **4** with 4,4′-dichlorobenzophenone in refluxing THF for 30 min gave 2-methyl-4-[bis(4-chlorophenyl)methylene]-4*H*-1-thianaphthalene (**6**), yield 78%, mp 158.5—159.5 °C (from MeOH); IR (KBr): 1480, 1095, 825, 760, and 750 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 1.99 (br s, 3H, 2-C-CH_3), 6.52 (br s, 1H, 3-CH), and 6.7—7.9 (m, 12H, aromatic); MS: *m/e* 398 (M^+ for two ^{37}Cl, 18%), 397 (20), 396 (M^+ for one ^{37}Cl and one ^{35}Cl, 72), 395 (31), 394 (M^+ for two ^{35}Cl, 100), 358 (M^+−HCl, 20), and 344 (358−CH_2, 17).

Found: C, 69.58; H, 3.84%. Calcd for $C_{23}H_{16}SCl_2$: C, 69.88; H, 4.08%.

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