Reactions of Aryliminotriphenylphosphoranes with Sulfenes

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Aryliminotriphenylphosphoranes reacted with methanesulfonyl, ethanesulfonyl and α-toluenesulfonyl chlorides in the presence of triethylamine to give 1 : 2 adducts [α-(*N*-alkanesulfonyl-*N*-arylsulfamoyl)alkylidenephosphoranes] and the decomposition products, instead of 1 : 1 adducts [α-(*N*-arylsulfamoyl)alkylidenephosphoranes). They were obtained under ice-cooling, the structure being of betaine type. In the case of methanesulfonyl chloride, isomeric 1 : 2 adduct [α-(*N*-arylsulfamoyl)methanesulfonylmethylenephosphorane] was also obtained. 2-Propanesulfonyl chloride gave *N*-triphenylphosphonio-*N*-arylsulfamate instead of expected adduct. In the absence of triethylamine, α-(*N*-arylsulfamoyl)alkyltriphenylphosphonium chlorides were obtained in good yields. Possible mechanisms of these reactions have been discussed.

In a previous paper,[1] we reported that reactions of arylimino- and acylmethylenetriphenylphosphoranes with benzenediazonium-2-carboxylate take place in a different manner. Ito *et al.*[2] reported the formation of alkanesulfonylmethylenephosphoranes (1 : 1 adduct) and episulfones or the decomposition products (*i.e.*, olefins) in the reactions of alkylidenephosphoranes with sulfene ($CH_2{=}SO_2$). Hamid and Trippett[3] obtained a similar 1 : 1 adduct in the reaction with phenylsulfene.

We have carried out the reactions of aryliminophosphoranes with sulfenes in order to compare them with reactions of alkylidenephosphoranes. Slightly different results were obtained.

Reactions with Unsubstituted Sulfene. When aryliminotriphenylphosphoranes (**1**) were allowed to react with two equivalents of sulfene generated from methanesulfonyl chloride (**2a**) and triethylamine at room temperature, *N*-aryl-*N*-methanesulfonylsulfamoylmethylenetriphenylphosphoranes (**3**), α-(*N*-arylsulfamoyl)-methanesulfonylmethylenetriphenylphosphoranes (**4**), which is an isomer of **3**, and triphenylphosphoniomethanesulfonate (**5**) were obtained in the yields shown in the following chart.

$$Ph_3P{=}N\text{-}Ar + 2\,MeSO_2Cl + 2\,Et_3N \rightarrow$$
1 **2a**

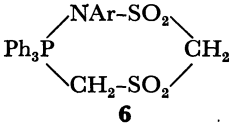
a, Ar=Ph
b, Ar=*p*-MeC_6H_4

$$Ph_3P{=}CHSO_2NAr\text{-}SO_2Me + Ph_3P{=}C(SO_2Me)SO_2NHAr + Ph_3\overset{+}{P}CH_2SO_3^-$$

	3	**4**	**5**
a	54%	38%	6%
b	38%	33%	16%

The structures of **3**, **4** and **5** were determined by elemental analyses, IR, NMR and MS spectra.

The NMR spectrum of **3a** showed a singlet peak at δ 3.20 ($MeSO_2$) and a doublet at δ 3.45 (J_{PCH} 12 Hz, disappeared by D_2O). The ^{31}P-NMR spectrum of **3b** exhibited a signal at δ_p −14.4 ppm (from 85% H_3PO_4 as an external standard). The data support the phosphorane structure (**3**), ruling out the exclusively cyclic structures **6** and **7**.



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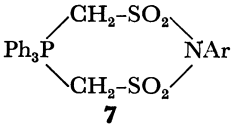

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The IR spectra of **4** showed an NH absorption band at about 3300 cm^{-1}.

The structures are also supported by the following reactions. By chromatography on silica gel, **3a** was partially hydrolyzed to triphenylphosphine oxide (**8**) and bis(methanesulfonyl)anilide (**9**), mp 195—196 °C, which was in agreement with that of an authentic sample prepared from aniline and excess of **2a**. Reaction of **3b** with *p*-nitrobenzaldehyde gave the corresponding olefin (**10**) and **8** in 38 and 41% yields, respectively.

$$p\text{-}NO_2C_6H_4\text{-}CH{=}CH\text{-}SO_2\text{-}N(SO_2Me)\text{-}C_6H_4Me\text{-}p$$
10

The presence of NH group in **4b** was confirmed by *N*-methylation to the *N*-methyl derivative (**11**).

$$Ph_3P{=}C(SO_2Me)\text{-}SO_2NMe\text{-}C_6H_4Me\text{-}p$$
11

The spectral data and melting point of **5** were in agreement with those of an authentic sample prepared from methylenetriphenylphosphorane with sulfur trioxide according to the method of Nesmeyanov *et al.*[4]

Equimolar reaction of **1a** and sulfene also gave 1 : 2 adducts (**3a** and **4a**) at room temperature, but a 1 : 1 adduct (**12a**) by slow addition of **2a** under cooling with ice. However, **12a** could not be obtained in a pure state, because of easy hydrolysis in solution to **8** and methanesulfonylanilide (**13a**).

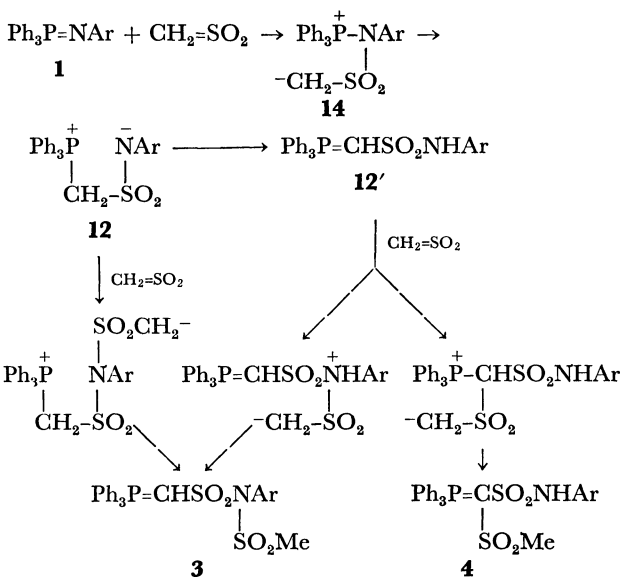
The MS spectrum of **12a** showed a parent peak at *m/e* 431. The absence of NH absorption band in the IR spectrum and the presence of a broad singlet at δ 4.30 (2H) in the NMR spectrum supported the betaine structure (**12a**) rather than a phosphorane structure (**12′a**).

$$Ph_3P{=}NPh + CH_2{=}SO_2 \rightarrow Ph_3\overset{+}{P}\text{-}\overset{-}{C}H_2SO_2NPh \xrightarrow{H_2O}$$
1a **12a**

$$Ph_3PO + MeSO_2NHPh \qquad Ph_3P{=}CHSO_2NHPh$$
8 **13a** **12′a**

Crude **12a** was allowed to react with sulfene to give 1 : 2 adducts **3a** and **4a** in 38 and 26% yields, respectively. The ratio of yield of **3a** to that of **4a** is 1.46, which is nearly equal to that in the above-mentioned 1 : 2 molar reaction (1.42). This indicates that **12a** is regarded as an intermediate in the formation of **3a** and **4a**.

Thus, the following mechanism is suggested.



The first step is supported by the fact that benzoyliminophosphorane did not react with sulfenes, because of the low electron density on the nitrogen atom.

On the other hand, the ratio of yield of **3b** to that of **4b** was 1.15 in the case of **1b**. This value was inconsistent with an expectation (above 1.42) on the basis of the presence of electron-donating methyl group, but the yield of **5** from **1b** was larger than that from **1a**. It is thus suggested that **5** is formed by the hydrolysis of **3b** during the treatment.

No nucleophilic attack of the carbanion center in **14** on the nitrogen atom gave triphenylphosphine and thiaziridine 1,1-dioxide or Schiff's base. This is a different case from that of alkylidenephosphoranes having no α-hydrogen,[2] and might be attributed to a greater stabilization of betaine (**12**) than that of carbon analogues, because of more electronegative nitrogen.

Reactions with Monosubstituted Sulfenes. Reaction of **1b** with phenylsulfene, generated from α-toluenesulfonyl chloride (**2b**) and triethylamine, gave 1 : 2 adduct (**3c**) and a betaine (**15c**) in 26 and 44% yields, respectively. Chromatography of the residue gave α-toluenesulfonyl-*p*-toluidide (**13c**) and **8** in 66 and 24% yields, respectively.

$$\underset{\mathbf{1}}{Ph_3P{=}NAr} + 2\,RCH_2SO_2Cl + 2\,Et_3N \rightarrow \underset{\mathbf{2}}{}$$

a, Ar=Ph b, R=Ph
b, Ar=*p*-MeC_6H_4 c, R=Me

$$Ph_3P{=}CR{-}SO_2NAr{-}SO_2CH_2R + RCH_2SO_2NHAr$$
3 **13**

c, Ar=*p*-MeC_6H_4, R=Ph;
d, Ar=Ph, R=Me

$$+\ Ph_3\overset{+}{P}{-}CHR{-}SO_3^- + Ph_3PO$$
15 **8**

c, R=Ph

Betaine (**15c**) precipitated from the filtrate on standing was insoluble in usual organic solvents, suggesting that it was formed during the treatment. Formation of **13c** and **8** also suggests that these compounds are hydrolyzed products of **3c**.

Thus, **3b** was heated in aqueous ethanol as a model compound, but was recovered unchanged. When hydrogen chloride gas was bubbled into **3b** in chloroform, **5** and **13b** (R=H, Ar=*p*-MeC_6H_4) were obtained almost quantitatively. Thus, it seems reasonable to consider that **5** or **15** and **13** are formed by acid-catalyzed hydrolysis of **3**, where acid is probably sulfonic acid produced during treatment. The first step is considered to be protonation at the α-carbon of **3b**, because the NMR spectrum of **3b** containing hydrogen chloride gas showed a doublet (δ 6.20, J_{PCH} 12 Hz) assignable to α-methylene protons of the corresponding phosphonium chloride, which is hydrolyzed easily because of the presence of positively charged phosphorus atom.

In the case of reaction of **1a** with methylsulfene, only 1 : 2 adduct (**3d**) was obtained in 34% yield as an identified product.

Reaction with Disubstituted Sulfene. Reactions of dimethylsulfene as a disubstituted sulfene with **1a** and **1b** gave only *N*-triphenylphosphonio-*N*-phenylsulfamate (**16a**) and -*N*-*p*-tolylsulfamate (**16b**) in 45 and 44% yields, respectively, as identified products.

$$\underset{\mathbf{1}}{Ph_3P{=}NAr} + Me_2C{=}SO_2 \rightarrow \underset{\mathbf{16}}{Ph_3\overset{+}{P}{-}NAr{-}SO_3^-}$$

a, Ar=Ph; b, Ar=*p*-MeC_6H_4

The structures were determined by elemental analyses, IR, ^{1}H- and ^{31}P-NMR spectra. The ^{1}H-NMR spectrum of **16b** showed A_2B_2 spin system (J 8.4 Hz) for four aromatic protons of *p*-tolyl group. The ^{31}P-NMR spectrum of **16a** showed a signal at δ_p −39 ppm, which is nearly equal to that of anilinotriphenylphosphonium chloride (δ_p −34 ppm[5]). However, **16** was stable against alkaline hydrolysis.

For the preparation of **16a**, **1a** was allowed to react with sulfur trioxide, but an isomeric betaine (**17**) was obtained in 58% yield. The alkaline hydrolysis gave sodium sulfanilate and **8**.

$$\underset{}{Ph_3P{=}NPh} + SO_3 \rightarrow \underset{\mathbf{17}}{Ph_3\overset{+}{P}{-}NHC_6H_4{-}SO_3^-{-}p}$$

The formation mechanism of **16** is obscure.

Reactions with Sulfonyl Chlorides in the Absence of Base. In the absence of triethylamine, reactions of iminophosphoranes (**1a,b**) with sulfonyl chlorides (**2a—c**) gave α-(*N*-arylsulfamoyl)alkyltriphenylphosphonium chlorides (**18**) in quantitative yields except for the case of **18c** (40% yield).

$$\underset{\mathbf{1}}{Ph_3P{=}NAr} + \underset{\mathbf{2}}{RCH_2SO_2Cl}$$

a, Ar=Ph a, R=H
b, Ar=*p*-MeC_6H_4 b, R=Ph

$$Ph_3\overset{+}{P}{-}NAr{-}SO_2CH_2R\ Cl^-$$
19

$$\longrightarrow \underset{\textbf{18}}{Ph_3\overset{+}{P}\text{-}CHRSO_2NHAr\ Cl^-}$$

a, Ar=Ph, R=H
b, Ar=Ph, R=Ph
c, Ar=Ph, R=Me
d, Ar=*p*-MeC$_6$H$_4$, R=H

The spectral data showed evidence that these products have structure **18** instead of the expected structure **19**[6] which was synthesized from triphenylphosphine and the corresponding *N*-chloroamide. Their IR spectra showed very broad NH absorption bands at 2700—2810 cm^{-1}, and their NMR spectra exhibited signals due to methine or methylene protons coupling with phosphorus nucleus.

Reaction of **1a** with **2b** gave **18b** and anilinotriphenylphosphonium chloride in 46 and 28% yields, respectively, under conditions similar to those in the case of **2a**. Thus, the reaction mechanism is considered to be as follows.

$$\underset{\textbf{1}}{Ph_3P{=}NAr} + \underset{\textbf{2}}{RCH_2SO_2Cl} \rightarrow \underset{Cl^-}{Ph_3\overset{+}{P}\text{-}NHAr} + RCH{=}SO_2$$

$$RCH{=}SO_2 \overset{\textbf{1}}{\rightarrow} Ph_3\overset{+}{P}\text{-}CHRSO_2\overset{-}{N}Ar \rightarrow \underset{\textbf{20}}{Ph_3P{=}CRSO_2NHAr}$$

$$\textbf{20} + \underset{}{Ph_3\overset{+}{P}NHAr\ Cl^-} \rightleftharpoons \underset{\textbf{18}}{Ph_3\overset{+}{P}\text{-}CHRSO_2NHAr\ Cl^-} + \textbf{1}$$

a, Ar=Ph
b, Ar=*p*-MeC$_6$H$_4$

Namely, **1** acts also as a base to generate sulfenes from **2**. In the case of **2b**, the basicity of the phosphorane (**20**) is weak because of α-phenyl group and attainment of the equilibrium in the last step becomes slow.

These reactions are the first example of reaction of aryliminophosphoranes with sulfonyl chlorides and may be synthetically useful because of high yield and easy treatment.

Experimental

All melting and boiling points were uncorrected. IR and MS spectra were measured with a Hitachi EPI-G2 spectrophotometer and a Hitachi RMU-6L mass spectrometer, respectively. ^{1}H-NMR spectra were measured with Hitachi R-20B, R-24 and R-22 spectrometers using TMS as an internal standard. ^{31}P-NMR spectra were measured with Hitachi R-20-R-204-P and R-20B-R-204-PB spectrometers using 85% phosphoric acid as an external standard.

Materials. Aryliminotriphenylphosphoranes were prepared by the method of Horner and Oediger[7]: phenylimino- (**1a**), mp 128—131 °C, and *p*-tolyliminotriphenylphosphoranes (**1b**), mp 133—136 °C.

Methanesulfonyl, α-toluenesulfonyl and 2-propanesulfonyl chlorides were prepared by the procedures given in literature: methanesulfonyl,[8] bp 154—158 °C, α-toluenesulfonyl,[9] mp 92 °C, and 2-propanesulfonyl chlorides,[10] bp 80 °C/20 mmHg. Commercial ethanesulfonyl chloride and triethylamine were used without further purification.

*Reactions of Methanesulfonyl Chloride (**2a**) in the Presence of Triethylamine. a) With Phenyliminotriphenylphosphorane (**1a**):* To **1a** (3.53 g, 10.0 mmol) and triethylamine (2.06 g, 20.3 mmol) in benzene (150 ml) was added dropwise **2a** (2.30 g, 20.2 mmol) in benzene (5 ml) with stirring at room temperature and the mixture was stirred overnight. The resulting precipitates were thoroughly washed with water and recrystallized from acetone to give **3a** (2.75 g, 54%), mp 198—199 °C(dec). IR (KBr): 1340, 1310 (*as*-SO_2), 1150 and 1130 cm^{-1} (*s*-SO_2); NMR ($CDCl_3$): δ 3.20 (s, 3H, SO_2Me), 3.45 (d, J_{PCH} 12 Hz, 1H, P=CH–, disappeared by D_2O), 7.0—7.2 (m, 5H, NPh), and 7.4—7.8 (m, 15H, Ph_3P).

Found: C, 61.42; H, 4.48; N, 2.82; S, 12.82%. Calcd for $C_{26}H_{24}NO_4PS_2$: C, 61.28; H, 4.75; N, 2.75; S, 12.58%.

Concentration of the mother liquor in the above recrystallization gave **4a**, mp 215—216 °C (dec) (from MeOH), yield 0.87 g. IR (KBr): 3300 (NH), 1335, 1285 (*as*-SO_2), 1150 and 1120 cm^{-1} (*s*-SO_2); NMR ($CDCl_3$): δ 2.98 (s, 3H, SO_2Me), 7.22 (s, 5H, NPh), and 7.38—7.73 (m, 15H, Ph_3P). No signal due to NH proton could be detected. HDO signal (1H) appeared at δ 4.65 by addition of D_2O.

Found: C, 61.28; H, 4.66; N, 2.59; S, 12.50%. Calcd for $C_{26}H_{24}NO_4PS_2$: C, 61.28; H, 4.75; N, 2.75; S, 12.58%.

From the filtrate of the reaction mixture, **5** precipitated on standing, mp 290—291 °C (from EtOH), yield 0.20 g (6%). IR (KBr): 1255 and 1240 cm^{-1} (SO_3^-); NMR (DMSO-d_6): δ 5.20 (d, J_{PCH} 13 Hz, 2H, CH_2), and 7.7—8.0 (m, 15H, Ph_3P).

Found: C, 63.97; H, 4.53; S, 9.06%; mol wt (Rast), 332. Calcd for $C_{19}H_{17}O_3PS$: C, 64.03; H, 4.81; S, 9.00%; mol wt, 356.

From the above filtrate, 1.07 g of **4a** was further obtained. Thus, the total yield of **4a** was 38%.

*b) With p-tolyliminotriphenylphosphorane (**1b**):* A similar reaction using **1b** (5.50 g, 15 mmol), Et_3N (3.23 g, 32 mmol), and **2a** (3.65 g, 32 mmol) in benzene (200 ml) gave **3b** (3.00 g, 38%), **4b** (2.60 g, 33%), and **5** (0.86 g, 16%).

3b: mp 188—189 °C (dec) (from acetone); IR (KBr): 1340, 1300 (*as*-SO_2), 1160 and 1130 cm^{-1} (*s*-SO_2); ^{1}H-NMR ($CDCl_3$): δ 2.76 (s, 3H, C_6H_4Me), 3.21 (s, 3H, SO_2Me), 3.49 (d, J_{PCH} 12 Hz, 1H, P=CH–), 6.94 (s, 4H, C_6H_4Me), and 7.4—7.8 (m, 15H, Ph_3P); ^{31}P-NMR (DMF): δ_p −14.4 ppm; MS: *m/e* 523 (M^+).

Found: C, 61.65; H, 4.86; N, 2.38; S, 12.08%. Calcd for $C_{27}H_{26}NO_4PS_2$: C, 61.95; H, 4.95; N, 2.68; S, 12.24%.

4b: mp 194—195 °C (dec) (from benzene); IR (KBr): 3260 (NH), 1320, 1290 (*as*-SO_2), 1135 and 1125 cm^{-1} (*s*-SO_2); NMR ($CDCl_3$): δ 2.32 (s, 3H, C_6H_4Me), 2.95 (s, 3H, SO_2Me), 7.10 (m, 4H, C_6H_4), and 7.3—7.8 (m, 15H, Ph_3P). Signal due to NH proton was obscure.

Found: C, 62.19; H, 4.65; N, 2.82; S, 12.28%. Calcd for $C_{27}H_{26}NO_4PS_2$: C, 61.95; H, 4.95; N, 2.68; S, 12.24%.

*Reaction of **1b** with α-Toluenesulfonyl Chloride (**2b**) in the Presence of Triethylamine.* To a solution of **1b** (4.40 g, 12.0 mmol) and Et_3N (2.54 g, 25.2 mmol) in benzene (200 ml) was added dropwise **2b** (5.01 g, 25.8 mmol) in benzene (100 ml) and the mixture was stirred for 10 hr at room temperature. The resulting precipitates were washed with water and recrystallized from acetonitrile and then acetone to give **3c** (2.12 g, 26%), mp 177 °C (dec). IR (KBr): 1350, 1265 (*as*-SO_2), 1190 and 1165 cm^{-1} (*s*-SO_2); NMR ($CDCl_3$): δ 2.05 (s, 3H, C_6H_4Me), 4.30 (s, 2H, SO_2CH_2), 6.60 (s, 4H, NC_6H_4Me), and 6.8—8.0 (m, 25H, 5Ph).

Found: C, 69.41; H, 4.83; N, 1.77; S, 9.75%. Calcd for $C_{39}H_{34}NO_4PS_2$: C, 69.31; H, 5.07; N, 2.07; S, 9.49%.

On being left to stand the filtrate gave **15c** (2.26 g, 44%), mp 280—282 °C (dec) (from acetonitrile). IR (KBr): 1250 and 1230 cm^{-1} (SO_3^-); NMR (DMSO-d_6): δ 6.70 (d, J_{PCH} 14 Hz, 1H, CH), 7.3—7.5 (m, 5H, CHPh), and 7.6—8.0 (m, 15H, Ph_3P).

An analytically pure sample could not be obtained, but

the structure was supported by the spectral data.

The filtrate was chromatographed on silica gel. Elution with benzene, benzene-ether and ethyl acetate-ethanol gave unchanged **2b** (0.40 g), **13c** (2.07 g, 66%), mp 113—114 °C (from EtOH) (lit,[11] 113 °C), and **8** (0.81 g, 24%), mp 153 °C (lit,[12] 156 °C), respectively.

*Reaction of **1a** with Ethanesulfonyl Chloride (**2c**) in the Presence Triethylamine.* Triethylamine (1.97 g, 18.3 mmol), **1a** (3.07 g, 8.7 mmol) and **2c** (2.48 g, 18.3 mmol) in benzene (100 ml) were allowed to react in a similar way, except for cooling with ice. The resulting precipitates were mainly triethylamine hydrochloride. After the solvent was removed from the filtrate, the residue was treated with ethanol to precipitate **3d**, mp 178 °C (from benzene), yield 1.58 g (34%). IR (KBr): 1335, 1300 (*as*-SO_2), 1160 and 1150 cm^{-1} (*s*-SO_2); NMR ($CDCl_3$): δ 1.41 (t, J 8 Hz, 3H, $SO_2CH_2CH_3$), 1.84 (d, J_{PCCH} 12 Hz, 3H, =CMe), 3.65 (q, J 8 Hz, 2H, SO_2CH_2), and 7.3—7.6 (m, 20H, Ph).

Found: C, 62.82; H, 5.46; N, 2.57; S, 12.18%. Calcd for $C_{28}H_{28}NO_4PS_2$: C, 62.55; H, 5.25; N, 2.61; S, 11.93%.

Reaction of 2-Propanesulfonyl Chloride in the Presence of Triethylamine. *a) With **1a**:* To a solution of **1a** (3.54 g, 10 mmol) and triethylamine (2.10 g, 20.8 mmol) in benzene (100 ml) was added dropwise 2-propanesulfonyl chloride (2.87 g, 20.1 mmol) in benzene (5 ml), and the mixture was stirred for two days. The resulting triethylamine hydrochloride (2.08 g, 71%) was filtered off and the filtrate was evaporated. After addition of benzene, recrystallization of the insoluble part from ethanol gave **16a** (1.94 g, 45%), mp 178—180 °C. IR (KBr): 1270 cm^{-1} (SO_3^-); ^{31}P-NMR (DMF): δ_p −39 ppm.

Found: C, 66.45; H, 4.61; N, 3.13; S, 7.68%. Calcd for $C_{24}H_{20}NO_3PS$: C, 66.50; H, 4.65; N, 3.23; S, 7.40%.

*b) With **1b**:* Triethylamine (2 ml), **1b** (1.84 g, 5.01 mmol) and the chloride (1.44 g, 10.1 mmol) were allowed to react in benzene in a similar manner.

16b: yield 1.00 g (44%); mp 181—182 °C (from EtOH); IR (KBr): 1275 cm^{-1} (SO_3^-); NMR (DMSO-d_6): δ 2.16 (s, 3H, C_6H_4Me), 6.90, 7.04, 7.17, 7.30, (A_2B_2, J 8.4 Hz, 4H, C_6H_4Me), and 7.5—8.1 (m, 15H, Ph_3P).

Found: C, 67.02; H, 5.00; N, 3.21; S, 7.30%. Calcd for $C_{25}H_{22}NO_3PS$: C, 67.10; H, 4.90; N, 3.13; S, 7.17%.

*Equimolar Reaction of **1a** with Sulfene.* To a solution of **1a** (3.51 g, 9.95 mmol) and triethylamine (1.5 ml) in benzene (100 ml) was added dropwise **2a** (1.14 g, 10.0 mmol) in benzene (10 ml) with stirring under cooling with ice and the mixture was stirred for 4 hr. The resulting precipitates were washed with water and dried quickly over phosphorus pentoxide to give **12a** (4.27 g, 99.5%). IR (KBr): 1290, 1255, 1165, and 1140 cm^{-1} (SO_2); NMR ($CDCl_3$): δ 2.90 (s, 0.6H, impurity, $PhNHSO_2Me$), 4.30 (broad s, 2H, P-CH_2SO_2, disappeared by D_2O), 7.1 (s, 5H, NPh), and 7.5—7.9 (m, 15H, Ph_3P); MS: *m/e* 431 (M^+). Addition of D_2O resulted in increase of the signal at 2.90.

The pure sample could not be obtained, because of easy hydrolysis in solution by moisture to **8** and **13a**. Thus, it was used for reactions without further purification.

*Reaction of **12a**.* *a) With Hydrogen Chloride*: Into a solution of **12a** (1.66 g, 3.86 mmol) in absolute methanol (50 ml) was bubbled dry hydrogen chloride for 1 hr. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel. Elution with chloroform-methanol (15 : 1) gave *N*-phenylsulfamoylmethylenetriphenylphosphonium chloride (1.07 g, 60%). The compound was recrystallized from ethanol. The spectra and melting point were in agreement with those of the sample obtained from **1a** and **2a**.

b) With Sulfene: To a suspension of **12a** (1.04 g, 2.4 mmol) and triethylamine (0.5 ml) in benzene (50 ml) was added dropwise **2a** (0.275 g, 2.4 mmol) in benzene (5 ml) and the mixture was stirred overnight. Washing of the resulting precipitates with water gave 0.30 g (0.59 mmol) of **3a**. Removal of the solvent from the filtrate and addition of ethanol afforded 0.49 g of precipitates, which were found to be a mixture of **3a** and **4a** by thin layer chromatography (tlc) and NMR spectrum. On the basis of the signal areas of methanesulfonyl protons in the NMR spectrum, the ratio of **3a** (δ 3.20) to **4a** (δ 2.98) was calculated to be 35/65. Thus, the total yields of **3a** and **4a** were 38 (0.47 g) and 26% (0.32 g), respectively.

*Wittig Reaction of **3b** with p-Nitrobenzaldehyde.* A mixture of **3b** (0.587 g, 1.12 mmol) and *p*-nitrobenzaldehyde (0.175 g, 1.15 mmol) in *o*-dichlorobenzene (50 ml) was heated at 150 °C for 32 hr under nitrogen. After filtration of precipitates and removal of the solvent from the filtrate, the residue was chromatographed on alumina. Fractions eluted with chloroform-benzene(3 : 5) gave 0.167 g (0.42 mmol, 38%) of **10**, mp 233—235 °C (from EtOH). IR (KBr): 1620 (C=C) 1510, 1370 (NO_2), 1350, 1330 (*as*-SO_2), 1160 and 1110 cm^{-1} (*s*-SO_2); NMR (DMSO-d_6): δ 2.35 (s, 3H, C_6H_4Me), 3.56 (s, 3H, SO_2Me), 7.32 (s, 4H, NC_6H_4Me), 7.71, 7.75 (2H), and 8.2—8.4 (m, 4H, $C_6H_4NO_2$); MS: *m/e* 396 (M^+).

Found: C, 48.78; H, 4.05; N, 6.81; S, 15.88%. Calcd for $C_{16}H_{16}N_2O_6S_2$: C, 48.48; H, 4.07; N, 7.07; S, 16.18%.

Elution with chloroform gave 0.129 g (0.46 mmol, 41%) of **8**.

*Methylation of **4b**.* Sodium hydride (45 mg) was added to a solution of **4b** (0.492 g, 0.94 mmol) in benzene (50 ml) and the mixture was stirred at room temperature for 1 hr. After addition of methyl iodide (1 ml), the mixture was refluxed overnight. After evaporation, the residue was washed with water and recrystallized from ethanol to give 0.345 g (68%) of **11**, mp 232—234 °C. IR (KBr): 1330, 1280 (*as*-SO_2), 1140 and 1120 cm^{-1} (*s*-SO_2); NMR ($CDCl_3$): δ 2.30 (s, 3H, C_6H_4Me), 2.95 (s, 3H, NMe), 3.30 (s, 3H, SO_2Me), 7.0—7.15 (m, 4H, C_6H_4Me), and 7.3—7.8 (m, 15H, Ph_3P); MS: *m/e* 537 (M^+).

Found: C, 62.29; H, 4.96; N, 2.43; S, 11.87%. Calcd for $C_{28}H_{28}NO_4PS_2$: C, 62.55; H, 5.25; N, 2.61; S, 11.93%.

*Preparation of **5**.* To a suspension of methyltriphenylphosphonium bromide (18 g, 50.4 mmol) in dioxane (80 ml) was added sodium hydride (1.5 g) under nitrogen, and the mixture was stirred for 1 hr. Filtration of sodium bromide and unchanged materials under nitrogen gave a solution of methylenetriphenylphosphorane. The solution was added dropwise to a suspension of sulfur trioxide-dioxane adduct[13] (14 g) in dioxane (80 ml) under nitrogen. The dioxane layer was separated off and the viscous liquid was chromatographed on silica gel. Elution with chloroform-methanol (15 : 1) gave 1 g (6%) of **5**, mp 290—291 °C (from EtOH).

*Reaction of **1a** with Sulfur Trioxide.* To a suspension of sulfur trioxide-dioxane adduct (10 g) in dichloromethane (30 ml) was added dropwise **1a** (8.39 g, 23.5 mmol) in dichloromethane (10 ml) and the mixture was stirred for 3 hr at room temperature. The resulting precipitates were recrystallized from methanol quickly, because of hygroscopic material, to give 5.955 g (58.4%) of **17** mp 276 °C (dec). IR (KBr): 2700 (NH) and 1230 cm^{-1} (SO_3^-); NMR ($HOCH_2CH_2OH$): 3.26, 3.40 (2H, half part of A_2B_2), 3.90, 4.0—4.6 (17H), and 4.70 ppm (broad s, 1H, NH), in low field from methylene signal of ethylene glycol.

Found: C, 66.54; H, 4.66; N, 3.07%. Calcd for $C_{24}H_{20}NO_3PS$: C, 66.50; H, 4.65; N, 3.23%.

*Hydrolysis of **3b**.* Into a solution of **3b** (0.53 g, 1.0 mmol) in chloroform (40 ml) was bubbled hydrogen chloride gas for 2 hr. After evaporation, the residue was chromatographed on silica gel to give **13b**, mp 101—102 °C (from EtOH) (lit,[14] 102.5 °C) with chloroform-methanol (19 : 1) and **5** with chloroform-methanol (5 : 1) almost quantitatively.

*Reactions of **1** with Sulfonyl Chloride (**2**) in the Absence of Triethylamine. a) Reaction of **1a** with **2a**:* A solution of **2a** (2.29 g, 2.01 mmol) in benzene (10 ml) was added dropwise to a solution of **1a** (7.05 g, 20.0 mmol) in benzene (100 ml) at room temperature under stirring and the mixture was stirred for 1 hr. The resulting precipitates were identified as **18a**, mp 122—124 °C (from acetone). Yield, quantitative. IR (KBr): 2700 (NH), 1350 and 1170 cm^{-1} (SO_2); NMR ($CDCl_3$): δ 5.86 (d, J_{PCH} 12 Hz, 2H, PCH_2SO_2), 7.15—8.0 (m, 20H, 4Ph), and 12.7 (very broad s, 1H, NH).

Found: C, 64.11; H, 5.17; N, 2.69; S, 6.93%. Calcd for $C_{25}H_{23}ClNO_2PS$: C, 64.17; H, 4.95; N, 2.99; S, 6.85%.

To **18a** (1.125 g, 24 mmol) in dichloromethane (50 ml) was added an excess of triethylamine, and the reaction mixture was subjected to silica gel dry column chromatography with ether after being stirred for 10 hr. Extraction of a part of R_f 0.6—0.8 with ether and recrystallization from ethanol gave 0.29 g (71%) of **13a**, mp 102 °C (lit,[14] 100.5 °C). Extraction of a part of R_f 0.2—0.5 with ethyl acetate gave 0.515 g (97%) of **8**.

*b) Reaction of **1a** with **2b**.* 1) A mixture of **1a** (3.56 g, 10.1 mmol) and **2b** (1.96 g, 10.3 mmol) was allowed to react similarly to give 3.83 g of precipitates. A part of the precipitates (1.60 g) was chromatographed on silica gel. Elution with chloroform-methanol (79 : 1) gave 1.07 g (46%) of **18b**, mp 150—151 °C (from ethanol-ether). IR (KBr): 2800 (NH), 1350 and 1160 cm^{-1} (SO_2); NMR ($CDCl_3$): δ 6.7—8.0 (m, 25H, 5Ph), 8.65 (d, J_{PCH} 16 Hz, 1H, P-CH-Ph), and 10.8 (very broad s, 1H, NH).

Found: C, 68.49; H, 4.86; N, 2.67; S, 5.99; Cl, 6.74%. Calcd for $C_{31}H_{27}ClNO_2PS$: C, 68.44; H, 5.00; N, 2.57; S, 5.89; Cl, 6.52%.

Elution of chloroform-methanol (3 : 1) gave 0.51 g (28%) of anilinotriphenylphosphonium chloride, mp 229—233 °C (lit,[15] 230—233 °C).

2) **1a** (3.55 g, 10.1 mmol) and **2b** (1.88 g, 9.87 mmol) were reacted in benzene (100 ml) for 3 days at room temperature to give **18b**, mp 150—151 °C, as precipitates quantitatively.

*Reactions of **1a** and **2c**.* **1a** (3.57 g, 10.1 mmol) and **2c** (1.31 g, 10.2 mmol) in benzene were allowed to react as in the case of **2a**. **18c** was obtained as precipitates, 1.97 g (40%), mp 180—185 °C (dec) (from acetone). IR (KBr): 2810 (NH), 1355 and 1170 cm^{-1} (SO_2); NMR ($CDCl_3$): δ 1.50 (d d, J_{PCCH} 18, J_{HH} 6 Hz, 3H, P-CHMe), 7.0—7.3 (m, 3H), 7.5—8.3 (m, 18H), and 11.75 (very broad s, 1H, NH). On addition of D_2O, the signal at δ 11.75 disappeared and double doublets at 1.50 changed to a doublet (J 18 Hz). Signal at 7.5—8.3 changed the peak area to 17H, indicating an overlap with methine proton.

Found: C, 64.81; H, 5.06; N, 2.71%. Calcd for $C_{26}H_{25}ClNO_2PS$: C, 64.79; H, 5.23; N, 2.91%.

*Reaction of **1b** and **2a**.* **1b** (3.657 g, 10.0 mmol) was allowed to react with **2a** (1.43 g, 9.98 mmol) as in the case of **2a** to afford **18d**, mp 166.7—168 °C (from acetone), quantitatively. IR (KBr): 2810 (NH), 1345 and 1165 cm^{-1} (SO_2); NMR ($CDCl_3$): δ 2.30 (s, 3H, C_6H_4Me), 5.91 (d, J_{PCH} 12 Hz, 2H, PCH_2SO_2), 7.01, 7.16, 7.50 (centered at 7.33) (A_2B_2, J 9 Hz, 3H, NC_6H_4Me), 7.6—8.2 (m, 16H, 3Ph and CH), and 10.57 (broad s, 1H, NH).

Found: C, 64.74; H, 5.31; N, 2.62%. Calcd for $C_{26}H_{25}ClNO_2PS$: C, 64.79; H, 5.19; N, 2.91%.

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References

1) T. Kawashima and N. Inamoto, This Bulletin, **45**, 3504 (1972).
2) Y. Ito, M. Okano, and R. Oda, *Tetrahedron*, **23**, 2137 (1967).
3) A. M. Hamid and S. Trippett, *J. Chem. Soc., C*, **1968**, 1612.
4) N. A. Nesmeyanov, S. T. Zhuzhlikova, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **151**, 856 (1963).
5) M. Yoshifuji, *Yuki Gosei Kagaku Kyokaishi*, **28**, 177 (1970).
6) V. A. Shokol, L. I. Molyavko, and G. I. Derkach, *Zh. Obshch. Khim.*, **36**, 930 (1966).
7) L. Horner and H. Oediger, *Ann. Chem.*, **627**, 142 (1959).
8) P. K. Dutt, *J. Chem. Soc.*, **125**, 1463 (1924).
9) T. B. Johnson and J. A. Ambler, *J. Amer. Chem. Soc.*, **36**, 372 (1914).
10) S. Zuffanti, *ibid.*, **62**, 1044 (1940).
11) E. Fromm and J. de Seixas Palma, *Ber.*, **39**, 3308 (1906).
12) C. Screttas and A. F. Isbell, *J. Org. Chem.*, **27**, 2573 (1962).
13) C. S. Rondestvedt, Jr. and F. G. Bordwell, "Organic Syntheses," Coll. Vol. 4, p. 846 (1963).
14) C. S. Marvel, M. D. Helfrick, and J. P. Belsley, *J. Amer. Chem. Soc.*, **51**, 1272 (1929).
15) R. D. Partos and K. W. Ratts, *ibid.*, **88**, 4996 (1966).