Organic and Biological Chemistry

Reactions of Phosphorus Compounds. XI. Geometry of Phosphorus Ylids

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X-Ray structures of three ylids, 2-chloro-2-(triphenylphosphoranylidene)acetophenone (I, X = Cl), 2-iodo-2-(triphenylphosphoranylidene)acetophenone (I, X = I), and p-tolyl 2-(triphenylphosphoranylidene)methyl sulfone (II, R = 4-CH₃C₆H₄) were determined. X-Ray studies confirmed, as previously suggested by spectral data, that the major contributing resonance structure is the dipolar betaine Ib. Carbanion stabilization by the sulfone group was shown to involve only the d orbitals of sulfur (IIc). The sulfonyl and carbonyl carbanions are all clearly sp², not sp³, hybridized. The phosphinemethylene P–C bond distance varies from 1.71 to 1.74 Å. Steric interactions between halogen and the phenacyl group in Ib are compensated by a distortion of the carbon–halogen bond length and of the planarity of the system. The observed geometry of these ylids allows an interpretation of reactivity in terms of steric factors.

The mechanism of the Wittig reaction has been reported for resonance-stabilized ylids.[1] The reaction is first order in ylid and aldehyde, $\rho = +2.7$ for a series of substituted aldehydes, $\Delta S^* \cong -40$ e.u. The rate increases with solvent polarity and the rate of disappearance of reactants is equal to the rate of formation of products. Assuming a steady-state approximation, one may arrive at the equation

rate of reaction = k_1(ylid)(aldehyde)/$(1 + k_{-1}/k_2)$

for the following sequence

$$\text{ylid} + \text{aldehyde} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{betaine} \overset{k_2}{\longrightarrow} \text{products}$$
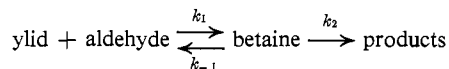
Study of the decomposition of the betaine intermediate, prepared *via* tertiary phosphines and epoxides, to ylid and aldehyde demands initial reversible nucleophilic attack of ylid upon aldehyde and indicates that generally $k_{-1} \cong k_2$. In many instances, then, the over-all rate and stereochemistry of the Wittig reaction depends upon k_1 to a large extent.

rate of reaction $\cong k_1$(ylid)(aldehyde)/2

It was, therefore, of interest to define some of the factors which are important in determining k_1.

The initial bimolecular, nucleophilic step of the Wittig reaction will be affected by electronic as well as steric factors. Hudson[2] has demonstrated a linear

relationship between ylid basicity and rate of reaction when hydrogen is attached to the methylenic carbon (I, X = H; C₆H₅ varied). When hydrogen is replaced by halogen, the linear relationship no longer holds and reactivity may be correlated with steric factors.[3] The ylids I where X = halogen are less reactive than those with X = hydrogen. Steric factors which may affect the initial nucleophilic attack make the geometry of these halo ylids important to the over-all rate of reaction.

We had previously proposed,[3] on the basis of infrared spectral data and observation of molecular models, that phenacyl ylids contain considerable carbon-carbon double-bond character as shown in Ib with the large triphenylphosphonium group and phenyl ring trans.
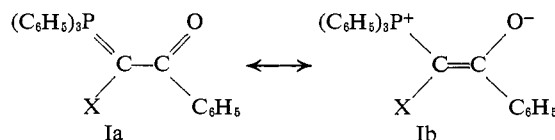
The decrease in basicity within the series of ylids I as X = I → Br → Cl is a result of a gain in planarity of the system, and hence carbanion delocalization, as X becomes smaller.[3] The rather high dipole moments of ylids also would suggest a dipolar structure such as Ib.[4] The contribution of Ib to the resonance hybrid is demonstrated by the O-alkylation of these species.[4]

An X-ray study of the crystal structure of three ylids was initiated to determine their geometry and to correlate this with previous reactivity, basicity, and spectral data.[5] The results for 2-chloro-2-(triphenylphosphoranylidene)acetophenone (I, X = Cl) and 2-iodo-2-(triphenylphosphoranylidene)acetophenone (I, X = I) are given in Figure 1 and Table I. The bromo ylid (I, X = Br) is isomorphous with the chloro ylid and thus has the same structure. The PC₁₉ bond distances are established at 1.736 ± 0.014 and 1.71 ± 0.05 Å. The C–O bond distances (1.301 ± 0.019 and 1.28 ± 0.06 Å.) are longer than an unconjugated carbonyl bond (acetone 1.14 Å.)[6] yet shorter than the carbon–oxygen

(1) A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 3878 (1963).

(2) S. Fliszar, R. F. Hudson, and G. Salvadori, *Helv. Chim. Acta*, **46**, 1580 (1963).

(3) A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **85**, 2790 (1963).

(4) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

(5) The geometry as determined by X-ray studies of the crystal structure may be extrapolated, to some extent, to the species in solution due to the similarity in the trends observed in the infrared spectra taken as mulls in Nujol and in chloroform solution. A detailed account of the X-ray study will be published elsewhere by Drs. P. J. Wheatley and F. S. Stephens.

(6) R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1960.
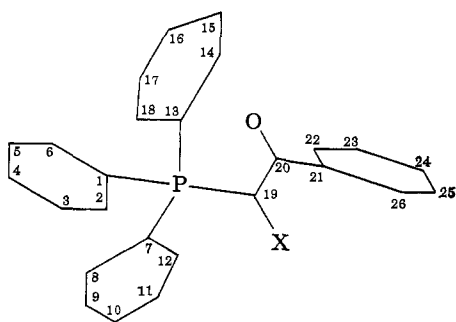
Figure 1. Molecular projection and carbon labeling of 2-chloro- and 2-iodo-2-(triphenylphosphoranylidene)acetophenone. The dihedral angle between $PC_{19}XC_{20}$ and $C_{19}C_{20}OC_{21}$ planes is 11° for X = I, 4.7° for X = Cl; between the C_{21} phenyl ring and the $C_{19}C_{20}OC_{21}$ plane, 51° for X = I, 57.6° for X = Cl.

bond in an enol ether (CH_2=$CHOCH_2CH_3$ 1.40 Å.). The central carbon C_{19} is sp^2 as indicated by the $ClC_{19}P$ (118.3°), $ClC_{19}C_{20}$ (121.2°), and $PC_{19}C_{20}$ (120.2°) angles and coplanarity of the four atoms Cl, P, C_{19},

Table I. Bond Lengths (Å.) and Bond Angles (deg)

2-Chloro-2-(triphenylphosphoranylidene)acetophenone			
ClC_{19}	1.759 ± 0.014	C_1PC_7	105.4 ± 0.6
OC_{20}	1.301 ± 0.019	C_1PC_{13}	108.9 ± 0.6
$C_{19}C_{20}$	1.361 ± 0.020	C_1PC_{19}	113.2 ± 0.6
$C_{20}C_{21}$	1.489 ± 0.020	C_7PC_{13}	106.4 ± 0.6
PC_{19}	1.736 ± 0.014	C_7PC_{19}	110.2 ± 0.6
PC_1	1.822 ± 0.014	$C_{13}PC_{19}$	112.3 ± 0.6
PC_7	1.798 ± 0.013	$ClC_{19}P$	118.3 ± 0.6
PC_{13}	1.800 ± 0.013	$ClC_{19}C_{20}$	121.2 ± 0.11
		$PC_{19}C_{20}$	120.2 ± 0.11
		$C_{19}C_{20}O$	116.6 ± 0.13
		$C_{19}C_{20}C_{21}$	126.0 ± 0.13
		$C_{21}C_{20}O$	117.2 ± 0.13
2-Iodo-2-(triphenylphosphoranylidene)acetophenone			
IC_{19}	2.19 ± 0.05	C_1PC_7	107 ± 3
OC_{20}	1.28 ± 0.06	C_1PC_{13}	106 ± 3
$C_{19}C_{20}$	1.35 ± 0.07	C_1PC_{19}	110 ± 3
$C_{20}C_{21}$	1.57 ± 0.08	C_7PC_{13}	107 ± 2
PC_{19}	1.71 ± 0.05	C_7PC_{19}	115 ± 2
PC_1	1.82 ± 0.07	$C_{13}PC_{19}$	112 ± 2
PC_7	1.77 ± 0.05	$IC_{19}P$	116 ± 2
PC_{13}	1.77 ± 0.05	$IC_{19}C_{20}$	$\ldots$
		$PC_{19}C_{20}$	120 ± 4
		$C_{19}C_{20}O$	115 ± 5
		$C_{19}C_{20}C_{21}$	128 ± 5
		$C_{21}C_{20}O$	117 ± 4
p-Tolyl 2-(triphenylphosphoranylidene)methyl sulfone			
SO_1	1.469 ± 0.014	O_1SO_2	117.4 ± 0.8
SO_2	1.444 ± 0.015	O_1SC_1	109.6 ± 0.8
SC_1	1.686 ± 0.019	O_2SC_1	110.9 ± 0.9
SC_2	1.767 ± 0.018	O_1SC_2	106.6 ± 0.8
PC_1	1.709 ± 0.019	O_2SC_2	104.7 ± 0.8
PC_8	1.832 ± 0.018	C_1SC_2	107.0 ± 0.9
PC_{14}	1.777 ± 0.016	PC_1S	123.9 ± 0.11
PC_{20}	1.815 ± 0.017	C_1PC_8	112.6 ± 0.9
		C_1PC_{14}	118.2 ± 0.8
		C_1PC_{20}	105.2 ± 0.8
		$C_{14}PC_{20}$	107.0 ± 0.8
		$C_{14}PC_8$	106.1 ± 0.8
		$C_{20}PC_8$	107.2 ± 0.8

and C_{20}. The triphenylphosphonium group and the phenyl ring are *trans* as predicted. The carbonyl group in Ib (X = I) is twisted 11° from the $PC_{19}X$ plane, whereas in Ib (X = Cl) it is twisted only 4.7°. The $C_{19}H_{20}$ distances approach those of a carbon-

carbon double bond in both cases (1.361 ± 0.020 and 1.35 ± 0.07 Å.) although the $C_{20}H_{21}$ phenyl distances are much longer (1.489 ± 0.020 and 1.57 ± 0.08 Å.). There is also a large departure from coplanarity of the carbonyl group and the phenyl ring in the two ylids and this is larger with the chloro ylid, 57.6°, than with the iodo ylid, 51°. The phenyl group, therefore, is not involved in any appreciable resonance interactions which stabilize the ylids. The carbon–halogen bond distances (CCl, 1.759 ± 0.014 and CI, 2.19 ± 0.05 Å.) are, within error, the same as in methyl halides (CCl, 1.77 and CI, 2.13 Å.) and are slightly lengthened compared to vinyl halides (CCl, 1.72 and CI, 2.03 Å.). The steric interference between X and COC_6H_5 groups is relieved by carbon–halogen bond lengthening and COC_6H_5 twisting from planarity. Since the phenyl ring is not an important factor in resonance stabilization, it may twist by a large angle to remove strain. Although the carbonyl may not twist from the plane of the $C_{19}H_{20}$ double bond to any appreciable extent, the reduction of coplanarity parallels an increase in the basicity of the ylid. The larger angle of twist for I, X = I (11°) compared to I, X = Cl (4.7°) would localize the negative charge at C_{19} to a greater extent and increase basicity. The effective bulk of the molecule is increased by the twisting to relieve strain, and with the large halogen atom attached to the reacting atom (C_{19}), steric requirements are great. This is evident in the observed reactivity of these ylids in the Wittig reaction.[3] The geometry of the ylids is the result of molecular compensation for internal strain by a preferred balance of carbon–halogen bond lengthening, a large reduction in the carbonyl–phenyl group planarity, and a small reduction in the carbon double-bond planarity.

An ylid stabilized by a sulfone group (II) was also of considerable interest.

(1) The replacement of the phenacyl group by an arylsulfonyl group decreases the reactivity of the ylid to p-nitrobenzaldehyde if X = H, and is unreactive if X = Br. Since a sulfone group ordinarily is worse than the carbonyl at stabilizing an adjacent carbanion,[7] it would appear that the decreased reactivity again might be due to steric factors. (2) Molecular orbital calculations by Koch and Moffitt[8] predict that "ordinary conjugation" with a sulfone group may occur with S–O lengthening if (a) the adjacent p orbital axis is perpendicular to the C_1SC_2 plane and (b) the sulfone is flanked by two unsaturated groups. The ν_{SO} stretch of II (R = CH_3) and II (R = 4-$CH_3C_6H_4$) is decreased in both from the ν_{SO} stretch of the corresponding salts (see Table II). However, in the first case (II, R = CH_3) only one attached group may conjugate with the sulfone moiety, suggesting that the above calculations are not applicable in these phosphorus ylids.

(3) Considerable discussion in recent literature[9] has also raised the question of sp^2 or sp^3 geometry for sulfonyl carbanions. For the above reasons, an X-ray study of p-tolyl 2-(triphenylphosphoranylidene)methyl sulfone was undertaken. The results are shown in Figure 2 and Table I. The PC_1 bond distance is

(7) R. G. Pearson and R. L. Dillon, J. Am. Chem. Soc., 75, 2439 (1953).
(8) H. A. Koch and W. E. Moffitt, Trans. Faraday Soc., 47, 7 (1951).
(9) See D. J. Cram, R. D. Trepka, and P. St. Janiak, J. Am. Chem. Soc., 86, 2731 (1964), for leading references.

Table II. Infrared SO_2 Stretching Frequencies (CHCl$_3$) for $(C_6H_5)_3P$=C(H)SO$_2$R and Their Salts

X	R	$\nu_{SO_2asym},$ cm.$^{-1}$	$\nu_{SO_2sym},$ cm.$^{-1}$	HBr salt, $\nu_{SO_2sym},$ cm.$^{-1}$	$\nu_{SO_2sym},$ cm.$^{-1}$
H	CH$_3$	1252	1112	1320	1148
H	4CH$_3$C$_6$H$_4$	1270	1130	1330	1165
Br	4CH$_3$C$_6$H$_4$	1270	1135	1335	1162

Figure 2. Molecular projection and carbon labeling of p-tolyl 2-(triphenylphosphoranylidene)methyl sulfone. The PC$_1$SO$_1$ atoms lie in the same plane and the tolyl ring at right angles to the C$_1$SC$_2$ plane.

1.709 ± 0.019 Å. The tolyl ring is perpendicular to the C$_1$SC$_2$ plane and the sulfone sulfur is tetrahedral. Although the central carbon is sp^2, or nearly so,[10] there is considerable steric hindrance introduced in line with decreased reactivity. Koch and Moffitt's calculations are conclusively demonstrated to be invalid in this case since the SO$_1$ bond is lengthened in the ylid compared to its salt[11] although the tolyl ring is perpendicular to the C$_1$SC$_2$ plane. The ultraviolet spectra of the ylids, $(C_6H_5)_3P$=CHSO$_2$CH$_3$, are also essentially identical (see Table III), indicating little through con-

Table III. Ultraviolet Spectra of $(C_6H_5)_3P$=CHSO$_2$R

| R	$\lambda_{max}^{CH_3OH}$ mμ	log ϵ
CH$_3$	223	4.10
	262	3.23
	267	3.32
	273	3.25
4-CH$_3$C$_6$H$_4$	223	4.24
	262	3.42
	267	3.48
	278	3.44

jugation with the d orbital of sulfur. The X-ray study also indicates that the carbanion stabilization is due mainly to the SO$_2$ group alone, since the SC$_2$ distance is nearly normal[12] (1.767 $\pm$ 0.018 Å.) and the SC$_1$ distance is much shorter (1.686 $\pm$ 0.019 Å.). There is some similarity to the previous study in that the P$^+$ and O$^-$ align and the central carbon (C$_1$) is sp^2. The structure suggests resonance stabilization primarily *via* sulfur and phosphorus d orbitals.

IIa ←→ IIb ←→

IIc
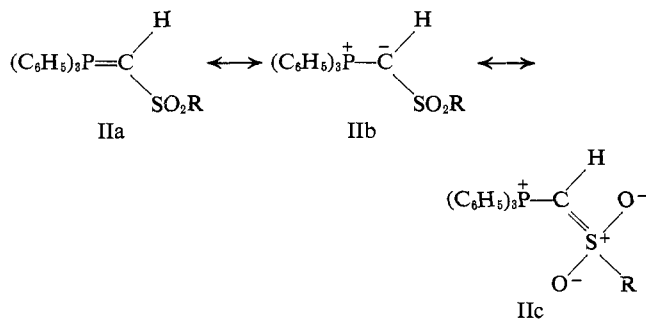
(10) The slight increase over 120° may be due to the electrostatic repulsion between positively charged phosphorus and sulfur.

(11) The decreased ν_{SO} of the ylids compared to the corresponding salts indicates the bond lengthening assuming the SO force constant does not change appreciably. Representative SO bond lengths are: CH$_3$-SO$_2$CH$_3$, 1.43 $\pm$ 0.02 Å. (R. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 53 (1950)) and (4-BrC$_6$H$_4$)$_2$SO$_2$, 1.54 $\pm$ 0.05 Å. (J. Toussaint, *Bull. soc. chim. Belges*, **54**, 319 (1945)).

(12) The references given in footnote 11 report the following values for carbon–sulfur bond distances: CH$_3$SO$_2$CH$_3$, 1.80 $\pm$ 0.02 and (4-Br-C$_6$H$_4$)$_2$SO$_2$, 1.84 $\pm$ 0.04 Å.
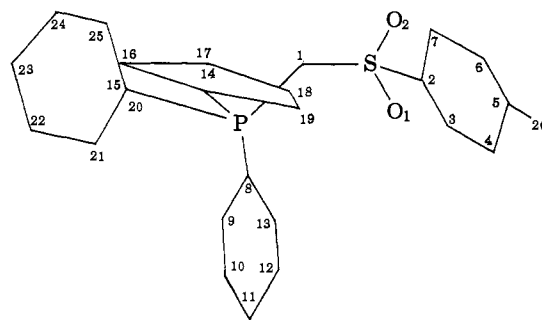
Such an effect, although much smaller, parallels that observed in the comparison of[13]
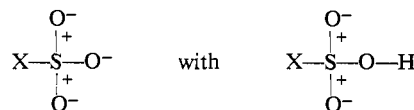
The difference is consistent with lesser double-bond character in the anion (see Table IV). The decrease in ν_{SO} which is also found in the ν_{CO} of carbonyl-stabilized ylids is due to a secondary effect upon the S–O bond, *i.e.*, the decrease in the positive charge on sulfur.

Table IV. Stretching Frequencies of S–O Bond

Compd.	$\nu_{SOsym},$ cm.$^{-1}$
FSO$_3$H	1230
FSO$_3^-$	1080
ClSO$_3$H	1209
ClSO$_3^-$	1054
HSO$_4$H	1195
HSO$_3^-$	1040

The postulated structure of P ylids based on spectral data is now confirmed by X-ray analysis. The P–C bond distance in P ylids is 1.71–1.74 Å. Stabilization of negative charge in these ylids appears to involve mainly the orbitals of atoms adjacent to the carbanion center. The central carbon is sp^2 and the structures tend to align P$^+$ and O$^-$ with the large groups *trans*. Basicity, reactivity, and spectral data can all be correlated with the X-ray determination of ylid structure to which Ib is the major contributing resonance form.

Experimental Section[14]

2-Iodo-2-(triphenylphosphoranylidene)acetophenone. This compound was prepared by the method of Speziale and Ratts.[3]

p-Tolyl 2-(Triphenylphosphoranylidene)methyl Sulfone. A mixture of bromomethyl p-tolyl sulfone (15.7 g., 0.63 mole) and triphenylphosphine (16.5 g., 0.63 mole) was heated to 110° for over 3 hr., and then to 155° for 22 hr. The mixture was allowed to cool and washed well with benzene. After drying, there was obtained 20.1 g. (62%) of crude product.

(13) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961).

(14) All melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Recrystallization of the salt from methylene chloride–benzene gave triphenyl(p-tolyl sulfonyl)methylphosphonium bromide, m.p. 267–270°. *Anal.* Calcd. for $C_{26}H_{23}BrO_2PS$: Br, 15.65; P, 6.07; S, 6.28. Found: Br, 15.77; P, 6.12; S, 6.34. The n.m.r. spectrum $(CDCl_3)$ is as follows: ArH, τ 2.25 (multiplet), $A = 21$; CH_2, 3.55 (doublet), $A = 2$; CH_3, 7.61 (singlet), $A = 3$. The infrared spectrum is given in Table II.

The above salt (20.1 g.) was added to water (700 ml.) at 60° and the mixture was filtered. The residual solid was washed with 300 ml. of water. The aqueous solution was treated with 1.0 N sodium hydroxide (100 ml.), and the precipitate was filtered and washed with water. The crude ylid was taken up in methylene chloride, dried over magnesium sulfate, and concentrated to 100 ml., and hexane was added to induce crystallization. A solid crystallized and was removed by filtration to give 11.2 g., m.p. 186–187°; 1.8 g., m.p. 160–170°; total yield, 76%. Recrystallization of the 11.2 g. of solid from methylene chloride–hexane gave m.p. 186–187°. *Anal.* Calcd. for $C_{16}H_{23}O_2PS$: C, 72.54; H, 5.38; S, 7.45; P, 7.20. Found: C, 72.21; H, 5.57; S, 7.67; P, 7.26. The infrared spectrum is given in Table II; the ultraviolet spectrum is given in Table III.

2-Bromo-2-(triphenylphosphoranylidene)methyl p-Tolyl Sulfone. This compound was prepared by the procedure of Speziale and Ratts[3] from p-tolyl (triphenylphosphoranylidene)methyl sulfone in 67% yield, m.p. 188–191°. *Anal.* Calcd. for $C_{26}H_{22}BrO_2PS$: Br, 15.69. Found: Br, 15.73. The infrared spectrum is given in Table II.

Methyl 2-(Triphenylphosphoranylidene)methyl Sulfone. [(Methylthio)methyl]triphenylphosphonium chloride was prepared according to the procedure of Wittig and Schlosser,[15] m.p. 218–220°. *Anal.* Calcd. for $C_{20}H_{20}ClPS$: C, 66.93; H, 5.62; Cl, 9.88; P, 8.63; S, 8.94. Found: C, 66.47; H, 6.10; Cl, 9.78; P, 8.69; S, 8.99.

The above salt (9.0 g., 0.025 mole) was dissolved in 60 ml. of glacial acetic acid–acetic anhydride (5:1) and hydrogen peroxide (35.0 g., 30% 0.55 mole) was added slowly at room temperature. The mixture was stirred for 14 hr., then heated on the steam bath for 45 min. at 95°. The mixture was cooled to 20° and anhydrous sodium sulfate added. After stirring for 10 min., the mixture was filtered and the residue was washed with glacial acetic acid. The solution was concentrated to a solid and extracted with methylene chloride (two 200-ml. portions). Concentration of this solution and recrystallization of the residue from

methylene chloride extraction gave triphenylphosphine oxide. The residue from the methylene chloride extractions was extracted with 200 ml. of water and made basic with 50% sodium hydroxide. The precipitate which formed was then taken up in $CHCl_3$ and crystallized with the addition of petroleum ether (b.p. 30–75°). This solid was recrystallized from chloroform–petroleum ether to give 0.3 g. (3.4%) of the desired ylid,[16] m.p. 200–203°. The infrared spectrum is given in Table II; the ultraviolet spectrum is given in Table III.

Other attempts to accomplish this oxidation with hydrogen peroxide, peracetic acid, and m-chlorobenzoic acid gave no ylid, only triphenylphosphine oxide.

Reaction of p-Tolyl 2-(Triphenylphosphoranylidene)-methyl Sulfone with p-Nitrobenzaldehyde. The ylid (2.15 g., 0.005 mole) and p-nitrobenzaldehyde (0.75 g., 0.005 mole) were dissolved in chloroform (50 ml.) and allowed to stand for 3 days at room temperature. The solution was concentrated *in vacuo.* Recrystallization of the residue gave 0.8 g. (53%) of the product, m.p. 183–184°. Recrystallization of this product from ethanol–chloroform gave 1-(p-nitrophenyl)-2-(p-tolylsulfonyl)ethylene, m.p. 185–186°. A mixture melting point with authentic material was not depressed. *Anal.* Calcd. for $C_{15}H_{13}NO_4S$: C, 59.40; H, 4.32; N, 4.62; S, 10.56. Found: C, 59.31; H, 3.82; N, 4.57; S, 10.49. Further concentration of the mother liquors and addition of hexane gave 0.9 g. (65%) of triphenylphosphine oxide.

1-p-Nitrophenyl)-2-(2-tolylsulfonyl)ethylene. p-Toluenesulfonylacetic acid (10.4 g., 0.049 mole) and p-nitrobenzaldehyde (7.6 g., 0.05 mole) were dissolved in piperidine (100 ml.) and heated to reflux for 2.5 hr. The mixture was poured onto 400 ml. of ice and allowed to stand for 1 hr. After filtration, the solid was washed with ethanol and recrystallized from hot ethanol–chloroform to give 3.0 g. of product, m.p. 182–184°. Recrystallization of this solid from ethanol–chloroform with charcoal treatment gave m.p. 184.5–185.5°.

2-Bromo-2-(triphenylphosphoranylidene)acetophenone gave a 64% yield of product after standing at room temperature for 24 hr. in chloroform. 2-Bromo-2-(triphenylphosphoranylidene)methyl p-tolyl sulfone, after standing for 3 days at room temperature in chloroform, did not react appreciably (by infrared analysis) with p-nitrobenzaldehyde.

Acknowledgment. We are extremely indebted to Drs. P. J. Wheatley and F. S. Stephens of Monsanto, Zurich, Switzerland, for their cooperation and determination of the X-ray structure of these ylids.

(15) G. Wittig and M. Schlosser, *Chem. Ber.*, 94, 1381 (1961).

(16) H. Hellman and J. Bader, *Tetrahedron Letters*, No. 20, 724 (1961).