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Reactions of Alkylidenetriphenylphosphoranes with Sulfur

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Reaction of diarylmethylenetriphenylphosphoranes with sulfur gave thiobenzophenones and triphenylphosphine sulfide in good yields. Reaction of benzylidenetriphenylphosphoranes with sulfur gave triphenylphosphine sulfide and 5,7-diphenyl-1,2,3,4,6-pentathiepane. More active alkylidenetriphenylphosphoranes such as isopropylidene- or *sec*-butylidenetriphenylphosphorane gave the corresponding phosphonium betaine containing sulfur atoms or phosphonium salt produced through air oxidation and hydrolysis of the betaine. α-Benzoylbenzylidenetriphenylphosphorane did not react with sulfur. Reactivity of alkylidenephosphoranes toward sulfur was briefly discussed.

Many examples are known on the formation of carbonyl or olefinic compounds by the reaction of alkylidenephosphoranes (I) with oxygen.[1–4] However, only a few examples have been reported on the reactions of I with sulfur,[5,6] although thiocarbonyl compounds could not be isolated.

We investigated the reaction of I with sulfur in more detail, in order to clarify this reaction.

Results and Discussion

Reaction of Diarylmethylenetriphenylphosphoranes (II). Phosphoranes (II) were prepared by adding the corresponding phosphonium bromide to sodium ethoxide in benzene or chlorobenzene, and were allowed to react with sulfur under reflux to give thiobenzophenones (III) and triphenylphosphine sulfide (IV) in good yields. Thiobenzophenones were identified by conversion into their phenylhydrazones. The results are summarized in Table 1.

Table 1. Reactions of II with sulfur

II	Solvent	III	(%)	Mp (Bp) (°C)	IV (%)
IIa	C_6H_6	IIIa	85	49—51	96
	C_6H_5Cl		80	(lit,[7] 53—54)	89
IIb	C_6H_6	IIIb	70[a]	71—76	69[a]
	C_6H_5Cl		52[a]	(lit,[8] 75—76)	62[a]
IIc	C_6H_6	IIIc	50[a]	85—87	67[a]
				(lit,[9] 90.5—91.5)	
IId	C_6H_6	IIId	70[a]	105—110	95[a]
				(lit,[9] 108.5—109.5)	
IIe	C_6H_6	IIIe	57[a]	(136—138/0.3 mmHg)	63[a]
	C_6H_5Cl		63[a]		67[a]
IIf	C_6H_6	IIIf	66[a]	(145—146/0.22 mmHg)	67[a]
	C_6H_5Cl		51[a]		66[a]

a) The yields were calculated on the basis of phosphonium salts used.

$$\underset{\text{II}}{Ph_3P{=}CArAr'} + S_8 \rightarrow \underset{\text{III}}{ArAr'C{=}S} + \underset{\text{IV}}{Ph_3P{=}S}$$

a: $Ar=Ar'=Ph$; b: $Ar=Ar'=p\text{-}MeC_6H_4$;
c: $Ar=Ar'=p\text{-}ClC_6H_4$; d: $Ar=Ar'=p\text{-}BrC_6H_4$;
e: $Ar=Ph$, $Ar'=p\text{-}MeC_6H_4$; f: $Ar=Ph$, $Ar'=p\text{-}ClC_6H_4$

Under the present conditions, thiobenzophenones did not react further with II to give olefinic compounds.

Reactions of Benzoylmethylenetriphenylphosphorane (V), α-Benzoylbenzylidenetriphenylphosphorane (VII) and Phenyliminotriphenylphosphorane. Benzoylmethylenetriphenylphosphorane (V) reacted easily with sulfur in refluxing benzene to give IV (88%) and an oily substance (VI), the structure of which corresponds to the trimer or tetramer of benzoylthioformaldehyde.

$$\underset{\text{V}}{Ph_3P{=}CH\text{-}COPh} + S_8 \rightarrow \underset{\text{IV}}{Ph_3P{=}S} + \underset{\text{VI }(n=3-4)}{(PhCOCHS)_n}$$

Desulfurization of VI with Raney Ni gave ethylbenzene and acetophenone which were identified by vapor phase chromatography (vpc). Distillation of VI gave only acetophenone.

The reaction of VII with sulfur was attempted in order to obtain monothiobenzil,[10] VII was recovered quantitatively.

$$\underset{\text{VII}}{Ph_3P{=}CPh(COPh)} + S_8 \rightarrow \text{no reaction}$$

Phenyliminotriphenylphosphorane did not react with sulfur in refluxing benzene even in the presence of basic catalysts.

Reaction of Benzylidenetriphenylphosphorane (VIII). The reaction of VIII with sulfur gave IV and a new compound (IX), $C_{14}H_{12}S_5$, in 83 and 14% yields in a short time, respectively. The prominent peaks in the MS spectrum of IX were m/e 340 (M^+, 4), 276 ($(PhCH)_2S_3^+$, 20), 220 ($PhCHS_4H_2^+$, 10), 219 ($PhCHS_4H^+$, 6), 218 ($PhCHS_4^+$, 48), 156 ($PhCHS_2H_2^+$, 12), 155 ($PhCHS_2H^+$, 35), 154 ($PhCHS_2^+$, 73), 153 ($PhCS_2^+$, 98), 124 ($PhCHSH_2^+$, 14), 123 ($PhCHSH^+$, 49), 122 ($PhCHS^+$, 93), 121 ($PhCS^+$, 100), 78 (PhH^+, 78) and 77 (Ph^+, 78).

$$\underset{\text{VIII}}{Ph_3P{=}CHPh} + S_8 \rightarrow \underset{\text{IV}}{Ph_3P{=}S} + \underset{\text{IX}}{(PhCH)_2S_5}$$

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[1] H. J. Bestmann, *Angew. Chem.*, **72**, 34 (1960).

[2] H. J. Bestmann and O. Kratzer, *ibid.*, **74**, 494 (1962).

[3] H. J. Bestmann and O. Kratzer, *Chem. Ber.*, **96**, 1899 (1963).

[4] H. J. Bestmann, H. Häberlein, H. Wagner, and O. Kratzer, *ibid.*, **99**, 2848 (1966).

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

[6] A. Schönberg, K. H. Brosowski, and E. Singer, *Chem. Ber.*, **95**, 2144 (1962).

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[9] A. Lüttringhaus and J. Grohmann, *Z. Naturforsh.*, **10b**, 365 (1955).

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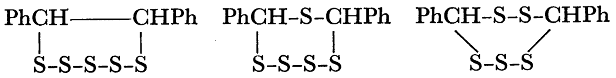
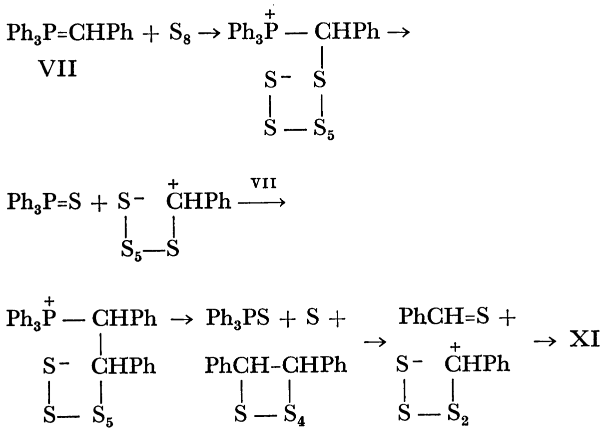
With regard to the structure of IX, three isomers, X, XI, and XII, are considered to be possible.


X XI XII

The structure X is excluded, because desulfurization of IX with Raney Ni gave no bibenzyl but toluene (58%). It is difficult to distinguish XI from XII with MS data, but the presence of the weak peak at *m/e* 212, which is attributable to stilbene episulfide, might favor XI to XII.

From the analogy of formation mechanism of ozonide,[11] the structure XI is also more favorable.



From the above facts, IX is tentatively assigned as 5,7-diphenyl-1,2,3,4,6-pentathiepane (XI).

Very recently, Mägerlein and Meyer have reported that arylmethylenetriphenylphosphoranes gave 1,2-diarylethylenes by reactions with sulfur at 100—120°C, and that triphenylphosphine sulfide and resinous material were obtained at 50—60°C.[12] In our case, a small amount of *cis*- and *trans*-stilbenes was also detected.

Reactions of Active Alkylidenephosphoranes. In the reaction of methylenetriphenylphosphorane (XIII) with sulfur at 70°C, brown precipitates appeared and unidentified gas evolved during the reaction. The gas reacted with metallic mercury but its structure could not be determined by means of IR spectrum. The brown precipitates gradually disappeared during the reaction and only IV was isolated in 74% yield after 6 hr.

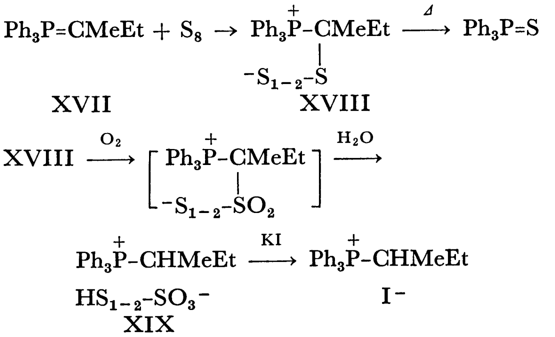
More active isopropylidenetriphenylphosphorane (XIV) gave large amounts of brown precipitates, which produced IV on heating at 200°C. During the usual treatment, the brown precipitates changed to phosphonium salt (XV), which possesses sulfonate group and gives isopropyltriphenylphosphonium iodide (XVI) with potassium iodide quantitatively. Absorptions at 1230, 1020, and 605 cm^{-1} in the IR spectrum of XV are consistent with those of sulfonate group.

$$\underset{\text{XIV}}{Ph_3P{=}CMe_2} + S_8 \rightarrow$$

$$\underset{\text{IV}}{Ph_3P{=}S} + \underset{\text{XV}}{\underset{(HS_{1-2}SO_3)^-}{Ph_3\overset{+}{P}\text{-}CHMe_2}} \xrightarrow{\text{KI}} \underset{\text{XVI}}{\underset{I^-}{Ph_3\overset{+}{P}\text{-}CHMe_2}}$$

In the case of *sec*-butylidenetriphenylphosphorane (XVII), large amounts of brown precipitates appeared in a similar way. The brown precipitates did not show absorptions attributable to sulfonate group in the IR spectrum, when the IR spectrum was measured immediately, but underwent oxidation and hydrolysis in air to give phosphonium salt (XIX), which possesses sulfonate group and also gives the corresponding iodide with potassium iodide.

Therefore, in the cases of the most active phosphoranes the reaction stopped at a stage of addition of sulfur to the P=C bond to give betaine (*e.g.*, XVIII), which is oxidized in air and hydrolyzed to form phosphonium salt possessing sulfonate group during the course of treatment.


$$\underset{\text{XVII}}{Ph_3P{=}CMeEt} + S_8 \rightarrow \underset{\text{XVIII}}{Ph_3\overset{+}{P}\text{-}CMeEt\text{-}S\text{-}S_{1-2}^-} \xrightarrow{\Delta} Ph_3P{=}S$$

$$\text{XVIII} \xrightarrow{O_2} \left[Ph_3\overset{+}{P}\text{-}CMeEt\text{-}SO_2\text{-}S_{1-2}^-\right] \xrightarrow{H_2O}$$

$$\underset{\text{XIX}}{\underset{HS_{1-2}\text{-}SO_3^-}{Ph_3\overset{+}{P}\text{-}CHMeEt}} \xrightarrow{\text{KI}} \underset{I^-}{Ph_3\overset{+}{P}\text{-}CHMeEt}$$

Reactivities of Phosphoranes toward Sulfur. The activity of phosphoranes used is considered to decrease in the following order:

$$\underset{\text{XVII}}{Ph_3P{=}CMeEt} \approx \underset{\text{XIV}}{Ph_3P{=}CMe_2} > \underset{\text{XIII}}{Ph_3P{=}CH_2} > \underset{\text{VIII}}{Ph_3P{=}CHPh} >$$

$$\underset{\text{II}}{Ph_3P{=}CArAr'} > \underset{\text{V}}{Ph_3P{=}CHCOPh} \gg \underset{\text{VII}}{Ph_3P{=}CPh(COPh)}$$

The most active phosphoranes (XIV and XVII) gave betaine with sulfur. The cleavage of the P=C bond scarcely occurred at 70—80°C. Phosphorane XIII also gave brown precipitates, which are considered to be betaine, but the precipitates disappeared after heating for a long period to produce triphenylphosphine sulfide, indicating that the cleavage of the P=C bond occurred very slowly.

The most stable phosphorane (VII) did not react with sulfur, and moderately active phosphoranes (VIII, II and V) underwent a cleavage of the P=C bond with sulfur easily.

Experimental

Materials. Diphenylmethylenetriphenylphosphorane (IIa) was prepared from diphenylmethyltriphenylphosphonium bromide and sodium ethoxide, mp 169—170°C (lit,[13] 174°C). Phosphonium salts were prepared from triphenylphosphine and the corresponding halides without solvent. They are summarized in Table 2.

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[11] a) P. Bailey, *Chem. Rev.* **58**, 925 (1958); b) A. P. Schaap and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 6055 (1970).

[12] H. Mägerlein and G. Meyer, *Chem. Ber.*, **103**, 2995 (1970).

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Table 2. Phosphonium salts (RPh$_3$P$^+$X$^-$) used

R	X	Mp (°C) (lit.)	Found (%)	
			C	H
Ph$_2$CH	Br	231—232 (230)13)		
(*p*-MeC$_6$H$_4$)$_2$CH	Br	200—203	73.59	5.70
(*p*-BrC$_6$H$_4$)$_2$CH	Br	226—230	55.72	3.65
(*p*-MeC$_6$H$_4$)PhCH	Br	230—235	73.38	5.41
(*p*-ClC$_6$H$_4$)PhCH	Br	227—228	68.24	5.10
(*p*-MeOC$_6$H$_4$)$_2$CH	Br	195—198	68.28	4.32
(*p*-ClC$_6$H$_4$)$_2$CH	Br	218.5—219	64.50	4.45
sec-Bu	I	204—205.5	59.00	5.44
i-Pr	I	192.7—194.7 (195—196)14)		
Me	Br	223—234 (232—233)15)		
PhCH$_2$	Br	231—232 (230)16)		

Benzoylmethylenetriphenylphosphorane (V) was prepared by the method of Ramirez,17) mp 180—181°C (lit, 178—180°C). α-Benzoylbenzylidenetriphenylphosphorane (VII) was prepared by the method of Trippett,18) mp 190.5—191.8°C (lit, 191—192°C). Phenyliminotriphenylphosphorane was prepared by the method of Staudinger,5) mp 129—131°C (lit, 131—132°C).

Reaction of Diphenylmethylenetriphenylphosphorane (IIa) with Sulfur. *a) In benzene*: A mixture of 23.4 g (0.055 mol) of IIa, 3.5 g (0.11 g atom) of sulfur, and 200 m*l* of dry benzene was heated at 80°C for one hour with stirring under nitrogen. The solvent was distilled off, and the residual blue oil was distilled at 104—107°C under a pressure of 0.5 mmHg. The deep violet distillate (IIIa) solidified, mp 49—51°C (mixt mp 49—51°C, lit,7) 53—54°C), yield 9.3 g (85%). Recrystallization of the residue of the distillation twice from ethanol gave triphenylphosphine sulfide (IV) (15.5 g, 96%), mp 156—158°C (lit,19) 157.5°C).

b) In Chlorobenzene: A mixture of 16.7 g (0.039 mol) of IIa, 2.54 g (0.078 g atom) of sulfur, and 150 m*l* of dry chlorobenzene was refluxed, and the reaction mixture was treated in a similar manner to that described in a) to give IIIa (6.2 g, 80%) and IV (10.2 g, 89%).

Reaction of Diarylmethylenetriphenylphosphoranes with Sulfur. A typical procedure is described for the reaction of di-*p*-tolylmethylenetriphenylphosphorane (IIb).

Sodium ethoxide was prepared from 1.17 g (0.051 g atom) of sodium metal and 100 m*l* of absolute ethanol. Ethanol was distilled off, and 400 m*l* of dry benzene was then added and about 100 m*l* of benzene was distilled off to remove ethanol as an azeotropic mixture. After the mixture was cooled to room temperature, 29.7 g (0.055 mol) of di-*p*-tolylmethyltriphenylphosphonium bromide was added. The color of the mixture slowly turned red. After one hour, the red solution was transferred through a G-4 glass-filter to a 500 m*l* three-necked flask, fitted with a reflux condenser, a gas-inlet tube and a stirrer under nitrogen. The filtrated red solution, 3.2 g (0.1 g atom) of sulfur was added. The mixture was then refluxed with stirring for one hour, during which the color of the reaction mixture turned blue rapidly. After the solvent was distilled off, the residual blue oil was distilled at 145—150°C under a pressure of 0.3 mmHg. The deep violet distillate (IIIb) (8.5 g, 70%) solidified, mp 71—76°C (lit,8) 75—76°C). From the residue of the distillation, 11.0 g (69%) of IV was obtained.

When chlorobenzene was used as a solvent instead of benzene, the yields of IIIb and IV were 52 and 62%, respectively, on the basis of di-*p*-tolylmethyltriphenylphosphonium bromide.

Reaction of Benzylmethylenetriphenylphosphorane (V) with Sulfur. a) A mixture of 9.5 g (0.025 mol) of V and 1.6 g (0.05 g atom) of sulfur and 40 m*l* of dry benzene was refluxed with stirring for one hour under nitrogen and the solvent was distilled off. The residual oil was chromatographed on silica gel. Elution with benzene-petroleum ether (3 : 7) gave white crystals after evaporation of the solvent. White crystals (IV) were recrystallized twice from ethanol, mp 155—158°C, yield 6.5 g (88%). Elution with benzene gave an orange oil (VI) after the evaporation of the solvent. Purification of the oil was unsuccessful. The yield was 3.0 g (80%). IR (neat): 1650 cm^{-1} (C=O); NMR (CDCl$_3$): τ 2.3—3.0 (5H, multiplet) and 5.82 (1H, singlet).

Found: C, 64.49; H, 3.89; S, 17.09%; mol. wt., 450—600 (by freezing point depression of benzene). Calcd for C$_8$H$_6$OS: C, 63.97; H, 4.03; S, 21.35%; mol. wt., 150.

A mixture of Raney Ni (W-7) prepared from 4 g of commercial Raney alloy and 0.5 g of the orange oil in 30 m*l* of ethanol was refluxed with stirring for 3 hr. From the filtrate, ethylbenzene and acetophenone were detected by vpc.

b) From the reaction mixture of 19 g (0.05 mol) of V and 3.2 g (0.1 g atom) of sulfur in 200 m*l* of dry benzene, the solvent was distilled off. The residual oil was distilled at 105°C under a pressure of 33 mmHg. The distillate (1.0 g, 17%) was identified as acetophenone by IR and vpc, but acetophenone was not detected from the reaction mixture by vpc.

Reaction of Methylenetriphenylphosphorane (XIII) with Sulfur. XIII was prepared from 19.1 g (0.054 mol) of methyltriphenylphosphonium bromide and sodium amide in liquid ammonia. Ammonia was then removed. After addition of 200 m*l* of dry benzene, the mixture was refluxed for one hour to remove ammonia completely, cooled and transferred to a separating funnel through a glass-filter. The solution was added dropwise to a mixture of 3.2 g (0.1 g atom) of sulfur and 300 m*l* of dry benzene at 70°C with stirring over 2 hr. During the reaction, brown precipitates appeared and a gaseous product which reacted with mercury metal was formed. When refluxing was continued for 6 hr the brown precipitates disappeared. After removal of the solvent the residual oil was chromatographed on silica gel. Elution with benzene - petroleum ether (1 : 1) gave IV (11.7 g, 74%).

Reaction of Benzylidenetriphenylphosphorane (VIII) with Sulfur. VIII prepared from 22.1 g (0.051 mol) of benzyltriphenylphosphonium bromide in liquid ammonia and sodium amide, was added dropwise to a solution of 3.2 g (0.1 g atom) of sulfur in 300 m*l* of dry benzene over a period of two hours at 70°C. The reaction mixture was cooled and the solvent was distilled off. The residual oil was chromatographed on silica gel. Elution with benzene - petroleum ether (1 : 10) gave white crystals after evaporation of the solvent. The white crystals (IX) were recrystallized twice from benzene - petroleum ether (1 : 1) and chloroform, mp 179—181.5°C. The crude yield was 1.23 g (14%).

Found: C, 49.23; H, 3.56; S, 46.67%; mol. wt., 351 (Rast), 340 (MS). Calcd for C$_{14}$H$_{12}$S$_5$: C, 49.37; H,

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15) G. Wittig and U. Schöllkopf, "Organic Syntheses" Vol. 40, p. 66 (1960).

16) M. Grayson and P. T. Keough, *J. Amer. Chem. Soc.*, **82**, 3919 (1960).

17) F. Ramirez and S. Derschowitz, *J. Org. Chem.*, **22**, 41 (1957).

18) S. Trippett and D. M. Walker, *J. Chem. Soc.*, **1961**, 1266.

19) A. Michaelis and L. Gleichmann, *Ber.*, **15**, 801 (1882).

3.55; S, 47.07%; mol wt, 340.

A mixture of Raney Ni (W-7), prepared from 2 g of commercial Raney alloy, 57 mg (0.168 mmol) of IX and 30 m*l* of ethanol was refluxed with stirring for 4 hr, and filtered. From the filtrate, toluene (58%) was detected by v.p.c.

Elution with benzene-petroleum ether (1 : 10) gave also a small amount of *trans*-stilbene, mp 122—124°C, and the presence of *cis*-stilbene was indicated by IR spectroscopy. Elution with benzene-petroleum ether (1 : 1) gave 12.5 g (83%) of IV.

Reaction of Isopropylidenetriphenylphosphorane (XIV) with Sulfur. XIV prepared from 25.9 g (0.06 mol) of isopropyltriphenylphosphonium iodide with sodium amide in liquid ammonia, was added dropwise to a solution of 4.0 g (0.12 g atom) of sulfur in 300 m*l* of dry benzene over a period of 3 hr at 70°C. Brown precipitates appeared and a gaseous product which reacted with mercury metal, evolved during the reaction. The reaction mixture was cooled and filtered. The brown precipitates which gave IV on heating to 200°C for 2 hr, were treated with active charcoal in ethanol several times to obtain white crystals (XV) (12.0 g, 46%), which were recrystallized three times from ethanol, mp 181—182.0°C.

Found: C, 57.32; H, 5.20; S, 19.30%. Calcd for $C_{21}H_{23}PO_3S_{2.65}$: C, 57.40, H, 5.28; S, 19.34%.

After removal of the solvent from the filtrate, IV (6.8 g, 38.5%) was obtained by silica gel chromatography. Compound (XV) (0.125 g, 0.28 mmol) in 20 m*l* of chloroform was stirred with 1.68 g of potassium iodide in 20 m*l* of water for 10 hr. Yellow crystals obtained from the organic layer were recrystallized twice from ethanol, and identified as isopropyltriphenylphosphonium iodide by comparison of its IR spectrum with that of an authentic sample and by mixed melting point (mp 195.5—196.5°C) with an authentic sample (lit,[14] 195—196°C). The yield was 0.102 g (81%). A mixture of XV (0.457 g, 1.04 mmol) and 6 m*l* of aqueous hydrogen iodide (57%) quickly turned red and black precipitates appeared and hydrogen sulfide evolved. The black precipitates consisted of iodine and isopropyltriphenylphosphonium iodide.

Reaction of sec-*Butylidenetriphenylphosphorane (XVII) with Sulfur.* XVII, prepared from 22.7 g (0.05 mol) of *sec*-butyltriphenylphosphonium iodide with sodium amide in liquid ammonia, was added dropwise to a solution of 3.2 g (0.1 g atom) of sulfur in 300 m*l* of dry benzene over a period of two hours at 70°C. Brown precipitates appeared and a gaseous product which reacted with mercury metal evolved during the reaction. The reaction mixture was cooled and filtered. The yield of brown precipitates was 8.0 g, mp 125—130°C (dec) and the IR spectrum exhibited the absence of sulfonate group. The brown precipitates which also gave IV on heating up to 200°C were treated with active charcoal in ethanol several times. White crystals (XIX) thus obtained were recrystallized three times from ethanol, mp 183.0—185.0°C, yield 7.7 g (33%).

Found: C, 58.38; H, 5.67; S, 18.64%. Calcd for $C_{22}H_{25}PO_3S_{2.65}$: C, 58.28; H, 5.56; S, 18.74%.

After removal of the solvent from the filtrate and chromatography on silica gel, elution with benzene-petroleum ether (1 : 1) gave IV (7.9 g, 54%). Compound (XIX) (0.117 g, 0.25 mmol) in 20 m*l* of chloroform was stirred with 1.17 g of potsssium iodide in 20 m*l* of water for 2 hr. Yellow crystals from the organic layer were recrystallized twice from ethanol-ether, and identified as *sec*-butyltriphenylphosphonium iodide. The yield was 83.4 mg (75%).