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The Reactions of Phosphonium Ylides and Oxosulfonium Methylide with Sulfenamide Derivatives

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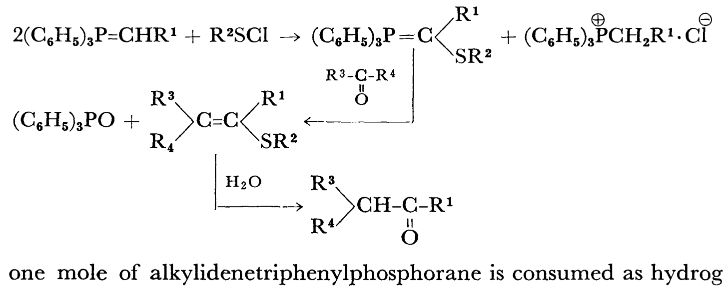
It was found that vinyl sulfide derivatives were obtained in good yields by the reactions of carbonyl compounds with α-phenylthioalkylidenetriphenylphosphorane. Phosphorane was prepared by the equimolar reaction of alkylidenetriphenylphosphorane and *N*-phenylthio-*N*-methylacetamide. It was established that, differing from the case of alkylidenetriphenylphosphorane, dimethyloxosulfonium methylide reacted with *N*-phenylthiophthalimide and *N*-phenylthiosuccinimide to give *N*-bis(phenylthio)methylphthalimide and *N*-bis(phenylthio)methylsuccinimide, respecitively.

It was recently reported that unsymmetrical ketones are synthesized in good yields *via* vinyl sulfide derivatives obtained from α-thioalkylidenetriphenylphosphorane and carbonyl compounds.[1] The phosphorane is successfully derived from 2 mol of alkylidenetriphenylphosphorane and 1 mol of sulfenyl chloride as shown in the following equation (1).



$$2(C_6H_5)_3P{=}CHR^1 + R^2SCl \rightarrow (C_6H_5)_3P{=}C{<}\begin{matrix}R^1\\SR^2\end{matrix} + (C_6H_5)_3\overset{\oplus}{P}CH_2R^1\cdot\overset{\ominus}{Cl} \qquad (1)$$

$$(C_6H_5)_3P{=}C{<}\begin{matrix}R^1\\SR^2\end{matrix} \xrightarrow{R^3\text{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}\text{-}R^4} (C_6H_5)_3PO + \begin{matrix}R^3\\R_4\end{matrix}{>}C{=}C{<}\begin{matrix}R^1\\SR^2\end{matrix}$$

$$\begin{matrix}R^3\\R_4\end{matrix}{>}C{=}C{<}\begin{matrix}R^1\\SR^2\end{matrix} \xrightarrow{H_2O} \begin{matrix}R^3\\R^4\end{matrix}{>}CH\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}R^1$$

In this reaction, one mole of alkylidenetriphenylphosphorane is consumed as hydrogen chloride scavenger to form phosphonium chloride.

We studied the reactions of alkylidenetriphenylphosphorane with sulfenamide derivatives with the

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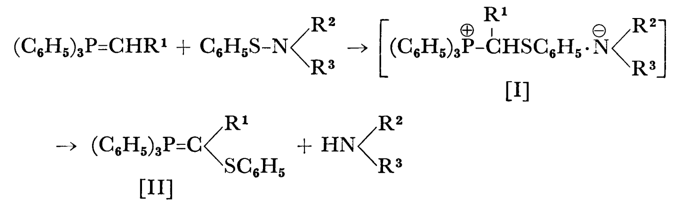
[1] T. Mukaiyama, S. Fukuyama and T. Kumamoto, *Tetrahedron Lett.*, **1968**, 3787.

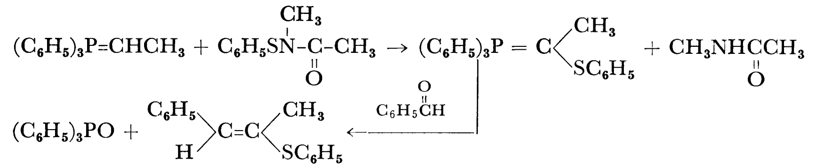
expectation that the equimolar reactions may proceed to give α-phenylthioalkylidenetriphenylphosphorane and amine, since the amido anion of initially formed phosphonium salt [I] may carry out the deprotonation from [I] to form corresponding phosphorane [II] (Eq. 2).



$$(C_6H_5)_3P{=}CHR^1 + C_6H_5S\text{-}N\begin{smallmatrix}R^2\\R^3\end{smallmatrix} \rightarrow \underset{[I]}{\left[(C_6H_5)_3\overset{\oplus}{P}\text{-}\overset{R^1}{C}HSC_6H_5\cdot\overset{\ominus}{N}\begin{smallmatrix}R^2\\R^3\end{smallmatrix}\right]}$$

$$\rightarrow \underset{[II]}{(C_6H_5)_3P{=}C\begin{smallmatrix}R^1\\SC_6H_5\end{smallmatrix}} + HN\begin{smallmatrix}R^2\\R^3\end{smallmatrix} \qquad (2)$$

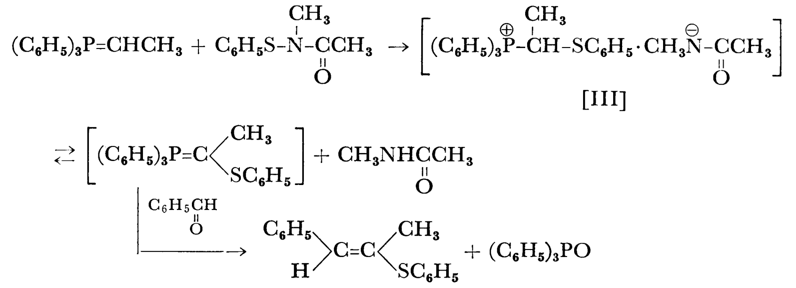
Benzenesulfenyl diethylamide did not react with ethylidenetriphenylphosphorane even after refluxing them in tetrahydrofuran, and benzenesulfenyl diethylamide was recovered quantitatively. On the other hand, it was established that when *N*-phenylthio-*N*-methylacetamide was treated with ethylidenetriphenylphosphorane at room temperature under nitrogen, a white precipitate deposited soon and β-methyl-β-phenylthiostyrene and triphenylphosphine oxide were obtained in 75% and 82% yields, respectively, by the subsequent reaction with benzaldehyde in refluxing tetrahydrofuran for 3 hr.



$$(C_6H_5)_3P{=}CHCH_3 + C_6H_5S\overset{CH_3}{N}\text{-}\underset{O}{\overset{\|}{C}}\text{-}CH_3 \rightarrow (C_6H_5)_3P = C\begin{smallmatrix}CH_3\\SC_6H_5\end{smallmatrix} + CH_3NH\underset{O}{\overset{\|}{C}}CH_3$$

$$(C_6H_5)_3PO + \begin{smallmatrix}C_6H_5\\H\end{smallmatrix}C{=}C\begin{smallmatrix}CH_3\\SC_6H_5\end{smallmatrix} \xleftarrow{C_6H_5\overset{O}{\overset{\|}{C}}H}$$

The white precipitate did not disappear in the absence of benzaldehyde even when it was refluxed for 5 hr in tetrahydrofuran. This suggests that the addition of benzaldehyde may shift equilibrium from the initially formed phosphonium salt [III] to the side of the α-phenylthioethylidenetriphenylphosphorane.



$$(C_6H_5)_3P{=}CHCH_3 + C_6H_5S\text{-}\overset{CH_3}{N}\text{-}\underset{O}{\overset{\|}{C}}CH_3 \rightarrow \underset{[III]}{\left[(C_6H_5)_3\overset{\oplus}{P}\text{-}\overset{CH_3}{C}H\text{-}SC_6H_5\cdot CH_3\overset{\ominus}{N}\text{-}\underset{O}{\overset{\|}{C}}CH_3\right]}$$

$$\rightleftarrows \left[(C_6H_5)_3P{=}C\begin{smallmatrix}CH_3\\SC_6H_5\end{smallmatrix}\right] + CH_3NH\underset{O}{\overset{\|}{C}}CH_3$$

$$\xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}H} \begin{smallmatrix}C_6H_5\\H\end{smallmatrix}C{=}C\begin{smallmatrix}CH_3\\SC_6H_5\end{smallmatrix} + (C_6H_5)_3PO$$

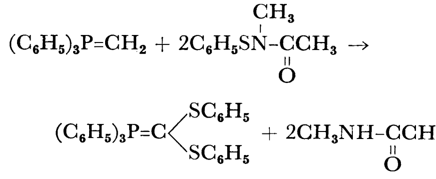
The reactions of α-phenylthioethylidenetriphenylphosphorane with *n*-butyraldehyde and acetophenone were also studied (see Table 1).

Table 1. The reactions of α-phenylthioethylidenetriphenylphosphorane with carbonyl compounds

Carbonyl compound	Thiovinyl ether Yield (%)	Thiovinyl ether Bp (°C/mmHg)	$OP(C_6H_5)_3$ Yield (%)
C_6H_5CHO	75	132/3	82
n-C_3H_7CHO	83	121/11	77
$C_6H_5COCH_3$	22	—*	57

* This compound was isolated by column chromatography.

It was found that bis(phenylthio)methylenetriphenylphosphorane was obtained in 98% yield by treating 1 mole of methylenetriphenylphosphorane with 2 moles of *N*-phenylthio-*N*-methylacetamide in tetrahydrofuran at room temperature under nitrogen.



$$(C_6H_5)_3P{=}CH_2 + 2C_6H_5S\overset{CH_3}{N}\text{-}\underset{O}{\overset{\|}{C}}CH_3 \rightarrow$$

$$(C_6H_5)_3P{=}C\begin{smallmatrix}SC_6H_5\\SC_6H_5\end{smallmatrix} + 2CH_3NH\text{-}\underset{O}{\overset{\|}{C}}CH_3$$

Sulfenamide derivatives were treated with dimethyloxosulfonium methylide in place of alkylidenetriphenylphosphorane. When dimethyloxosulfonium methylide was treated with *N*-phenylthiophthalimide[2] in boiling tetrahydrofuran for 6 hr under nitrogen, *N*-bis(phenylthio)methylphthalimide was obtained in 41% yield instead of dimethyloxosulfonium phenylthiomethylide expected from the reaction of the alkylidenetriphenylphosphorane with sulfenamide mentioned above.

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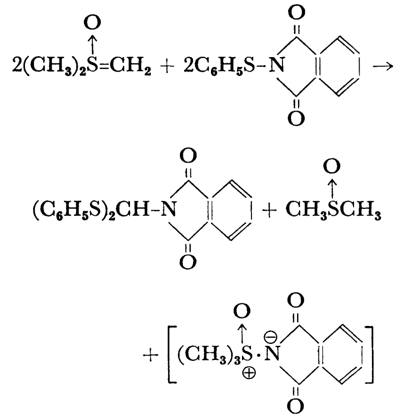
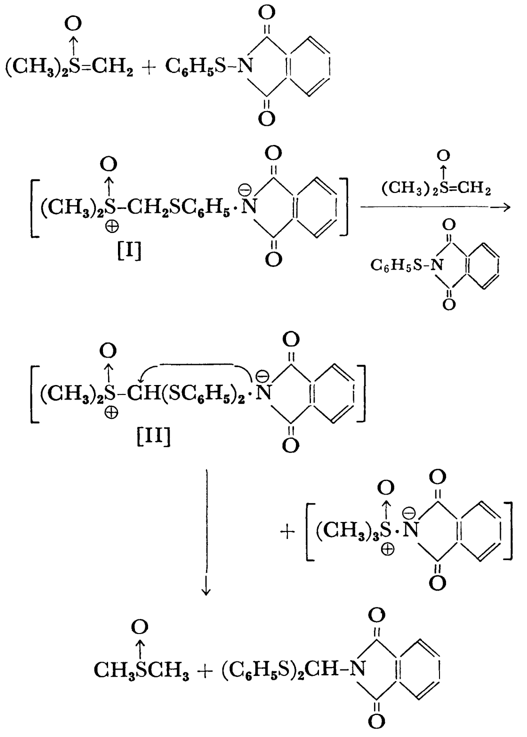
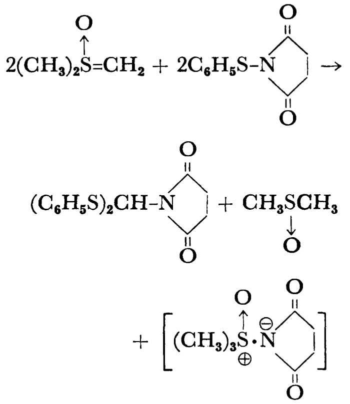
2) M. Behforouz and J. E. Kerwood, *J. Org. Chem.*, **34**, 51 (1969).



The unexpected formation of *N*-bis(phenylthio)methylphthalimide may be explained by considering an initial formation of oxosulfonium salt [I] from equimolar amounts of dimethyloxosulfonium methylide and *N*-phenylthiophthalimide. Salt [I] rapidly reacts with one mole of dimethyloxosulfonium methylide and one mole of *N*-phenylthiophthalimide to give oxosulfonium salt [II]. Salt [II] thus formed affords *N*-bis(phenylthio)methylphthalimide and dimethyl sulfoxide by the nucleophilic attack of the phthalimide anion to the α-carbon atom of the salt [II] as sketched below.

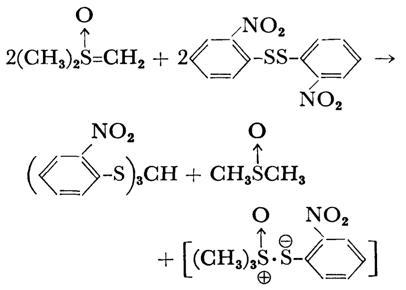


Similarly, *N*-bis(phenylthio)methylsuccinimide was obtained in 42% yield by the reaction of *N*-phenylthiosuccinimide[2] with dimethyloxosulfonium methylide in boiling tetrahydrofuran.

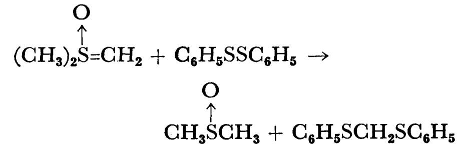


Benzenesulfenyl diethylamide did not react with dimethyloxosulfonium methylide even after refluxing them in tetrahydrofuran for 10 hr and the starting materials were recovered quantitatively.

It was found that the reaction of dimethyloxosulfonium methylide with bis(2-nitrophenyl) disulfide in tetrahydrofuran at room temperature gave tris(2-nitrophenylthio)methane in 77% yield.

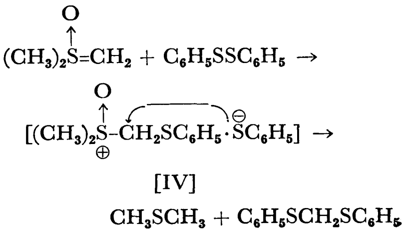


In the reaction of diphenyl disulfide with dimethyloxosulfonium methylide in boiling tetrahydrofuran, bis(phenylthio)methane was obtained in 51% yield.



$$(CH_3)_2\overset{O}{\overset{\uparrow}{S}}{=}CH_2 + C_6H_5SSC_6H_5 \rightarrow CH_3\overset{O}{\overset{\uparrow}{S}}CH_3 + C_6H_5SCH_2SC_6H_5$$

This suggests that the nucleophilic attack of phenylthio anion on the α-carbon atom of the oxosulfonium salt [IV] to form bis(phenylthio)methane is much faster than the reaction of [IV] with the oxosulfonium methylide to form tris(phenylthio)methane through dimethyloxosulfonium phenylthiomethylide.



$$(CH_3)_2\overset{O}{\overset{\uparrow}{S}}{=}CH_2 + C_6H_5SSC_6H_5 \rightarrow [(CH_3)_2\underset{\oplus}{\overset{O}{\overset{\uparrow}{S}}}\text{-}CH_2SC_6H_5\cdot\overset{\ominus}{S}C_6H_5] \rightarrow$$

[IV]

$$CH_3SCH_3 + C_6H_5SCH_2SC_6H_5$$

Experimental

Synthesis of *N*-Phenylthio-*N*-methylacetamide. Into a solution of sodium salt of *N*-methylacetamide, formed from *N*-methylacetamide (7.30 g, 0.10 mol) and sodium ethoxide, in tetrahydrofuran, benzenesulfenyl chloride (14.45 g, 0.10 mol) was added dropwise under stirring at room temperature. After stirring for 1 hr at room temperature, the solvent was evaporated under reduced pressure. The residue was added into 100 m*l* of water and the mixture was extracted with ether. After removal of ether, *N*-phenylthio-*N*-methylacetamide was obtained by distillation under reduced pressure, 11.13 g (62%) bp 96°C/2 mmHg.

Reaction of *N*-Phenylthio-*N*-methylacetamide with Ethylidenetriphenylphosphorane. *N*-Phenylthio-*N*-methylacetamide (1.10 g, 0.0065 mol) was added into a solution of ethylidenetriphenylphosphorane, formed from triphenylethylphosphonium bromide (2.41 g, 0.0065 mol) and *n*-butyl lithium (0.0065 mol), in tetrahydrofuran under stirring. Following the addition of *N*-phenylthio-*N*-methylacetamide, a white precipitate was obtained. Into the reaction mixture, benzaldehyde (0.69 g, 0.0065 mol) was added under stirring. The white precipitate disappeared by refluxing for 2 hr. After removal of the solvent, the residue was chromatographed on silica gel with benzene and ether, *β*-phenylthio-*β*-methylstyrene, 1.10 g (75%), bp 130—132°C/3 mmHg and triphenylphosphine oxide, 1.48 g (53%), mp 153—155°C, were obtained from the elute with benzene and ether, respectively.

Similarly, 2-phenylthio-2-hexene and 2-phenylthio-3-phenyl-2-butene were obtained by the reaction of α-phenylthioethylidenetriphenylphosphorane with *n*-butyraldehyde and acetophenone, respectively. The results are listed in Table 1.

Reaction of Methylenetriphenylphosphorane (1 mol) with *N*-Phenylthio-*N*-methylacetamide (2 mol). A solution of *N*-phenylthio-*N*-methylacetamide (1.81 g, 0.01 mol) in tetrahydrofuran was added into the solution of methylenetriphenylphosphorane (0.005 mol) in tetrahydrofuran under stirring. The reaction mixture was stirred for 1 hr at room temperature. After removal of the solvent, a crystalline solid precipitate was obtained by the addition of ethanol to the residue. Recrystallization from a mixture of benzene and ethanol gave bis(phenylthio)methylenetriphenylphosphorane, 2.40 g (98%), mp 165°C.

Reaction of Dimethyloxosulfonium Methylide with *N*-Phenylthiophthalimide. Into a solution of *N*-phenylthiophthalimide (2.55 g, 0.01 mol) in tetrahydrofuran, dimethyloxosulfonium methylide[3] (0.01 mol) was added under nitrogen. The reaction mixture was refluxed for 6 hr under stirring. After removal of the solvent, phthalimide (0.84 g, quantitatively) was obtained as white crystalline solid by the addition of a mixture of benzene and ether. The residue was chromatographed on silica gel with benzene. From the elute of benzene, *N*-bis(phenylthio)methylphthalimide was obtained by recrystallization from ethanol, 0.77 g (41%), mp 164—165°C. Found: C, 67.07; H, 3.89; N, 3.82; S, 16.76%. Calcd for $C_{21}H_{15}NO_2S_2$: C, 66.84; H, 4.01; N, 3.71; S, 16.96%.

Similarly, *N*-bis(phenylthio)methylsuccinimide was obtained by the reaction of dimethyloxosulfonium methylide with *N*-phenylthiosuccinimide, 42%, mp 94—95°C.

Found: C, 62.64; H, 4.36; N, 4.17; S, 19.70%. Calcd for $C_{17}H_{15}NS_2O_2$: C, 62.00; H, 4.59; N, 4.25; S, 19.43%.

Reaction of Dimethyloxosulfonium Methylide with Bis(2-nitrophenyl) Disulfide. Dimethyloxosulfonium methylide (0.01 mol) was added to a solution of bis(2-nitrophnyl) disulfide (3.08 g, 0.01 mol) in tetrahydrofuran under stirring. After stirring for 3 hr at room temperature, the solvent was evaporated under reduced pressure. A yellow crystalline was obtained by the addition of a small amount of ether to the residue. Recrystallization of the crystalline solid from ethanol gave tris(2-nitrophenylthio)methane 1.82 g (77%) mp 198—199°C.

Reaction of Dimethyloxosulfonium Methylide with Diphenyl Disulfide. Into a solution of diphenyl disulfide (2.18 g, 0.01 mol) in tetrahydrofuran, dimethyloxosulfonium methylide (0.01 mol) was added under stirring. The reaction mixture was refluxed for 2 hr. After removal of the solvent, the residue was chromatographed on silica gel with benzene. From the elute with benzene, bis(phenylthio)methane was obtained by distillation under reduced pressure, 1.19 g (51%), bp 170—175°C/0.7 mmHg.

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3) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).