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New Syntheses of Vinyl Sulfides and Unsaturated Nitriles *via* Quaternary Phosphonium Salts

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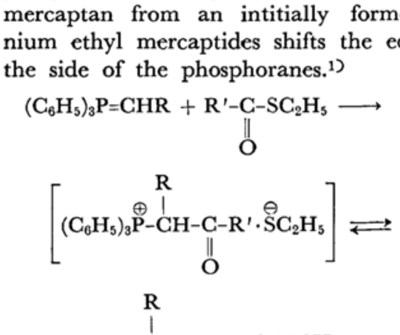
New methods for the syntheses of vinyl sulfides and unsaturated nitriles *via* quaternary phosphonium salts have been established. The reaction of isopropylidenetriphenylphosphorane with *S*-ethyl thiobenzoate or substituted *S*-ethyl thiobenzoates afforded vinyl sulfides and triphenylphosphine oxide in good yields. Further, it was found that the reaction of α-benzoylalkylphosphonium salts with sodium ethylmercaptide or potassium cyanide gave olefins, such as vinyl sulfides or unsaturated nitriles, and triphenylphosphine oxide in good yields, respectively.

The reaction of alkylidenephosphoranes with *S*-ethyl thiocarboxylate affords acylalkylidenephosphoranes in high yields. A removal of ethylmercaptan from an intitially formed phosphonium ethyl mercaptides shifts the equilibrium to the side of the phosphoranes.[1]

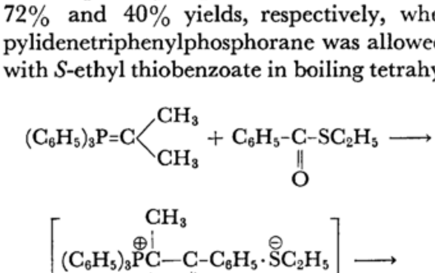


$$(C_6H_5)_3P{=}CHR + R'\text{-}\underset{\underset{O}{\|}}{C}\text{-}SC_2H_5 \longrightarrow$$

$$\left[(C_6H_5)_3\overset{\oplus}{P}\text{-}\overset{\overset{R}{|}}{C}H\text{-}\underset{\underset{O}{\|}}{C}\text{-}R'\cdot\overset{\ominus}{S}C_2H_5\right] \rightleftarrows$$

$$(C_6H_5)_3P{=}\overset{\overset{R}{|}}{C}\text{-}\underset{\underset{O}{\|}}{C}\text{-}R' + C_2H_5SH$$

It was found by the present experiment that the reaction of thiolester with alkylidenephosphoranes having no hydrogen atom on the methylene carbon resulted in the formation of the Wittig type reaction products, vinyl sulfides and triphenylphosphine oxide. Thus, 1-ethylthio-2-methyl-1-phenylpropene and triphenylphosphine oxide were obtained in 72% and 40% yields, respectively, when isopropylidenetriphenylphosphorane was allowed to react with *S*-ethyl thiobenzoate in boiling tetrahydrofuran.



$$(C_6H_5)_3P{=}C\begin{matrix}CH_3\\CH_3\end{matrix} + C_6H_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}SC_2H_5 \longrightarrow$$

$$\left[(C_6H_5)_3\overset{\oplus}{P}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{—}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5\cdot\overset{\ominus}{S}C_2H_5\right] \longrightarrow$$

(I)

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{=}C\!<\!\!\begin{matrix}C_6H_5\\SC_2H_5\end{matrix} + (C_6H_5)_3PO$$

Similarly, isopropylidenetriphenylphosphorane reacted with *S*-methyl thiobenzoate and substituted *S*-ethyl thiobenzoates, such as *S*-ethyl *p*-chlorothiobenzoate and *S*-ethyl *p*-methoxythiobenzoate,

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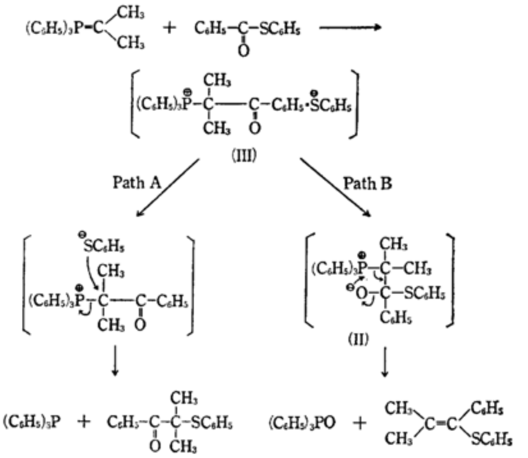
1) a) H. J. Bestmann and B. Arnason, *Chem. Ber.*, **95**, 1513 (1962). b) H. J. Bestmann and B. Arnason, *Tetrahedron Letters*, **1961**, 455.

Table 1. The reaction of isopropylidenetriphenylphosphorane with thiolester

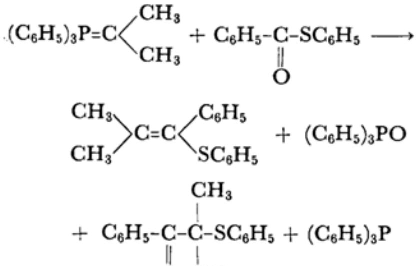
Thiolester	Vinyl sulfide Yield (%)	Bp °C/mmHg	Anal. Found (Calcd) C(%)	Anal. Found (Calcd) H(%)	$(C_6H_5)_3PO$ (%)
$C_6H_5COSC_2H_5$	72	134—136/28	75.16 (74.97	8.58 8.39)	40
$C_6H_5COSCH_3$	73	118/16	73.87 (74.13	7.89 7.92)	45
p-$ClC_6H_4COSC_2H_5$	83	147/15	63.75 (63.72	6.95 6.67)	52
p-$CH_3OC_6H_4COSC_2H_5$	70	154/16	70.35 (70.24	8.13 8.16)	52

to give corresponding vinyl sulfides and triphenylphosphine oxide in good yields (see Table 1).

The above mentioned reactions are considered to proceed through an initial formation of phosphonium mercaptide (I). An intramolecular nucleophilic attack of the ethylmercapto anion on carbonyl carbon of (I) yields the vinyl sulfide and triphenylphosphine oxide probably through a betain structure (II) as shown in path B of the following scheme.



On the contrary, vinyl sulfide was not obtained when isopropylidenetriphenylphosphorane and *S*-phenyl thiobenzoate were refluxed in tetrahydrofuran. Instead, only phosphonium phenylmercaptide resulted. The phosphonium salt decomposed to yield 2-methyl-1-phenyl-1-phenylthiopropene (14%), triphenylphosphine oxide (10%), α-phenylthioisobutyrophenone (28%) and triphenylphospine (36%) when it was refluxed in toluene.



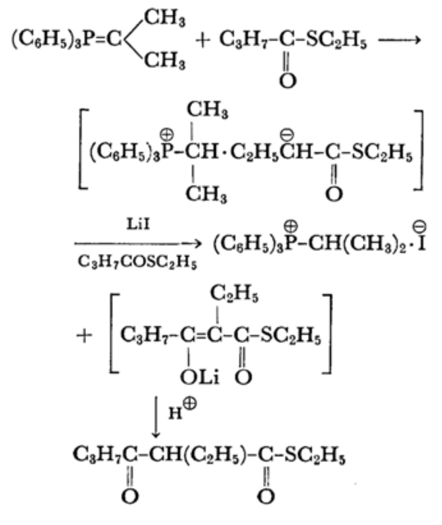
$$(C_6H_5)_3P{=}C\begin{matrix}CH_3\\CH_3\end{matrix} + C_6H_5\text{-}\underset{\overset{\|}{O}}{C}\text{-}SC_6H_5 \longrightarrow$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}C{=}C\begin{matrix}C_6H_5\\SC_6H_5\end{matrix} + (C_6H_5)_3PO$$

$$+ C_6H_5\text{-}\underset{\overset{\|}{O}}{C}\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}SC_6H_5 + (C_6H_5)_3P$$

The formation of α-phenylthioisobutyrophenone and triphenylphosphine can be explained by assuming a nucleophilic attack of phenylmercapto anion on the α-carbon of the phosphonium salt (III) (Path A). It is noteworthy that, in the case of the *S*-phenyl thiocarboxylate, the nucleophilic attack of reference anion, phenylmercapto anion, occurs competitively on α-carbon and on carbonyl carbon to afford the above mentioned four products.

In the case of the reaction of isopropylidenetriphenylphosphorane with *S*-ethyl thiobutyrate in tetrahydrofuran, triphenylisopropylphosphonium iodide (99%) and *S*-ethyl α-butyrylthiobutyrate (77%) were obtained. This result shows that ester condensation reaction of *S*-ethyl thiobutyrate preferentially takes place to afford α-butyrylthiobutyrate by the influence of isopropylidenetriphenylphosphorane, a strong basic substance. The formation of triphenylisopropylphosphonium iodide can be explained by assuming the anion exchange reaction of phosphonium salt (IV) with lithium iodide.



$$(C_6H_5)_3P{=}C\begin{matrix}CH_3\\CH_3\end{matrix} + C_3H_7\text{-}\underset{\overset{\|}{O}}{C}\text{-}SC_2H_5 \longrightarrow$$

$$\left[(C_6H_5)_3\overset{\oplus}{P}\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}H}\cdot C_2H_5\overset{\ominus}{C}H\text{-}\underset{\overset{\|}{O}}{C}\text{-}SC_2H_5\right]$$

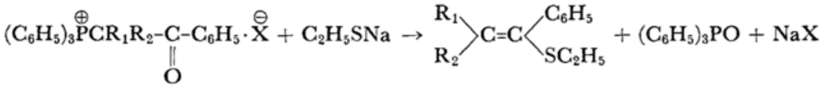
$$\xrightarrow[C_3H_7COSC_2H_5]{LiI} (C_6H_5)_3\overset{\oplus}{P}\text{-}CH(CH_3)_2\cdot\overset{\ominus}{I}$$

$$+\left[C_3H_7\text{-}\underset{\underset{OLi}{|}}{C}{=}\overset{\overset{C_2H_5}{|}}{C}\text{-}\underset{\overset{\|}{O}}{C}\text{-}SC_2H_5\right]$$

$$\Big\downarrow H^{\oplus}$$

$$C_3H_7\underset{\overset{\|}{O}}{C}\text{-}CH(C_2H_5)\text{-}\underset{\overset{\|}{O}}{C}\text{-}SC_2H_5$$

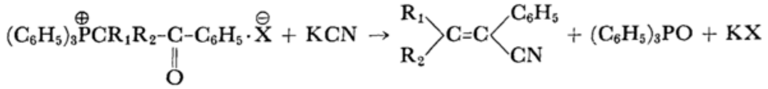
TABLE 2. THE REACTION OF α-BENZOYLALKYLPHOSPHONIUM SALT WITH SODIUM ETHYL MERCAPTIDE



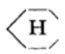
$$(C_6H_5)_3\overset{\oplus}{P}CR_1R_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5\cdot\overset{\ominus}{X} + C_2H_5SNa \rightarrow \begin{matrix}R_1\\R_2\end{matrix}\!\!>C=C<\!\!\begin{matrix}C_6H_5\\SC_2H_5\end{matrix} + (C_6H_5)_3PO + NaX$$

R_1	R_2	Vinyl sulfide				$(C_6H_5)_3PO$ (%)
		Yield (%)	Bp (mp) °C/mmHg	Anal. Found (Calcd) C(%)	H(%)	
CH_3	CH_3	52	130/20	—	—	67
		45	150—155/7	77.87 (77.55	8.67 8.68)	47
CH_3	C_6H_5	83	113—115/1 (54)	79.78 (80.28	7.32 7.13)	82

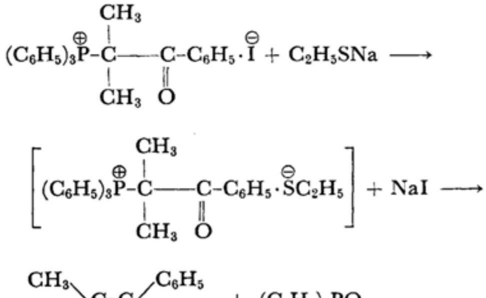
TABLE 3. THE REACTION OF α-BENZOYLALKYLPHOSPHONIUM SALT WITH POTASSIUM CYANIDE



$$(C_6H_5)_3\overset{\oplus}{P}CR_1R_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5\cdot\overset{\ominus}{X} + KCN \rightarrow \begin{matrix}R_1\\R_2\end{matrix}\!\!>C=C<\!\!\begin{matrix}C_6H_5\\CN\end{matrix} + (C_6H_5)_3PO + KX$$

R_1	R_2	Unsaturated nitrile					$(C_6H_5)_3PO$ (%)
		Yield (%)	Bp (mp) °C/mmHg	Anal. Found (Calcd) C(%)	H(%)	N(%)	
CH_3	CH_3	54	124—125/3	83.51 (84.04	7.06 7.05	8.86 8.91)	52
		72	116—117/1	85.33 (85.23	7.37 7.66	6.93 7.10)	82
CH_3	C_6H_5	75	(81)	87.47 (87.64	5.73 5.98	6.63 6.39)	82

Next, the isolation of the key intermediate (I) of the above mentioned reactions forming vinyl sulfide from sodium ethylmercaptide and triphenyl-α-benzoylisopropylphosphonium iodide was attempt. When sodium ethylmercaptide and triphenyl-α-benzoylisopropylphosphonium iodide, formed from isopropylidenetriphenylphosphorane and benzoyl chloride,[2] were refluxed in tetrahydrofuran for 6 hr, 1-ethylthio-2-methyl-1-phenylpropene (52%) and triphenylphosphine oxide (67%) were obtained as expected.



$$(C_6H_5)_3\overset{\oplus}{P}\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{---}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5\cdot\overset{\ominus}{I} + C_2H_5SNa \longrightarrow$$

$$\left[(C_6H_5)_3\overset{\oplus}{P}\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{---}\underset{\underset{O}{\|}}{C}\text{-}C_6H_5\cdot\overset{\ominus}{S}C_2H_5\right] + NaI \longrightarrow$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=C<\!\!\begin{matrix}C_6H_5\\SC_2H_5\end{matrix} + (C_6H_5)_3PO$$

Similarly, the reaction of triphenyl-α-benzoylcyclohexylphosphonium bromide or triphenyl-1-benzoyl-1-phenylethylphosphonium bromide with sodium ethylmercaptide resulted in the formation of corresponding α-ethylthiobenzylidenecyclohexane or 1,2-diphenyl-1-ethylthiopropene and triphenylphosphine oxide in good yields (see Table 2). It is of interest to note that α-ethylthiobenzylidenecyclohexane could not be obtained directly from *S*-ethyl thiobenzoate and cyclohexylidenetriphenylphosphorane because the phosphonium salt, the key intermediate, could not be obtained even when they were refluxed in tetrahydrofuran.

In addition, it was found that the reaction of triphenyl-α-benzoylalkylphosphonium salt with sodium phenylmercaptide or potassium thiocyanate did not afford the expected olefins, such as vinyl sulfides or vinyl thiocyanates.

Finally, this reaction was successfully extended to the synthesis of unsaturated nitriles by reacting triphenyl-α-benzoylalkylphosphonium salts with potassium cyanide. When triphenyl-α-benzoylisopropylphosphonium iodide was allowed to react with potassium cyanide in tetrahydrofuran - water mixed solvent at room temperature, α-phenyl-β-methylcrotonitrile (54%) and triphenylphosphine oxide (52%) were obtained.

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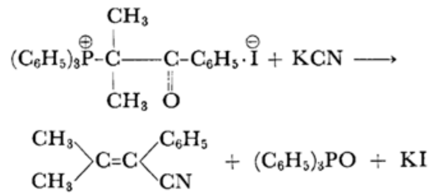
[2] H. J. Bestmann and T. Denzel, *Tetrahedron Letters*, **1966**, 3591.



$$(C_6H_5)_3\overset{\oplus}{P}\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{—}\underset{O}{\overset{}{C}}\text{-}C_6H_5\cdot\overset{\ominus}{I} + KCN \longrightarrow$$

$$(CH_3)_2C{=}C(C_6H_5)(CN) + (C_6H_5)_3PO + KI$$

In a similar manner, cyclohexylidenephenylacetonitrile or α,β-diphenylcrotonitrile was obtained by the reaction of triphenyl-α-benzoylcyclohexylphosphonium bromide or triphenyl-1-benzoyl-1-phenylethylphosphonium bromide with potassium cyanide in good yields (see Table 3).

Further study on this type of the synthesis of unsaturated compound is now in progress.

Experimental

Reaction of Isopropylidenetriphenylphosphorane with *S*-Ethyl Thiobenzoate. *S*-Ethyl thiobenzoate (1.33 g, 0.008 mol) was added to the solution of isopropylidenetriphenylphosphorane, prepared from triphenylisopropylphosphonium iodide (4.32 g, 0.01 mol) and *n*-butyl lithium (0.01 mol) in tetrahydrofuran (20 m*l*) under nitrogen. The dark red color disappeared soon and a phosphonium salt precipitated. The reaction mixture was further refluxed for 4 hr under stirring. After resulted precipitate was filtered, the filtrate was evaporated under reduced pressure. The distillation *in vacuo* gave 1-ethylthio-2-methyl-1-phenylpropene (1.14 g, 74%), bp 133—135°C/25 mmHg. The precipitate and the residue of the distillation were collected and refluxed in a mixture of aqueous solution of 5% sodium hydroxide (10 m*l*) and benzene (10 m*l*) for 30 min. After precipitated triphenylisopropylphosphonium iodide was filtered, the benzene layer was separated. The removal of benzene gave white crystals. They were recrystallized from carbon tetrachloride, triphenylphosphine oxide was obtained, 1.20 g (40%), mp 154—156°C.

Reaction of Isopropylidenetriphenylphosphorane with *S*-Phenyl Thiobenzoate. A mixture of isopropylidenetriphenylphosphorane (0.02 mol) and *S*-phenyl thiobenzoate (4.28 g, 0.02 mol) was refluxed in toluene for 5 hr. After resulting precipitate was filtered, the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel with petroleum ether, benzene and ether. α-Phenylthioisobutyrophenone, 1.00 g (25%) and triphenylphosphine oxide, 0.43 g (10%), mp 155—156°C, along with a mixture of triphenylphosphine and 2-methyl-1-phenyl-1-phenylthiopropene (V) were obtained from the elutate with benzene, ether and petroleum ether, respectively. α-Phenylthioisobutyrophenone was identified by the formation of its 2,4-dinitrophenylhydrazone, mp 155—156°C.

Found: C, 60.19; H, 4.73; N, 12.88%. Calcd for $C_{22}H_{20}N_4O_4S$: C, 60.54; H, 4.62; N, 12.84%. The mixture of triphenylphosphine and V was treated with an excess amount of methyl iodide to give triphenylmethylphosphonium iodide, 2.02 g. From the yield of phonium iodide, the yield of triphenylphosphine was estimated, 31%. The residue was distilled *in vacuo* to give V, 0.53 g (14%), bp 118—120°C/3 mmHg.

Reaction of Isopropylidenetriphenylphosphorane with *S*-Ethyl Thiobutyrate. A mixture of isopropylidenetriphenylphosphorane (0.01 mol) and *S*-ethyl thiobutyrate (1.32 g, 0.01 mol) in tetrahydrofruan (20 m*l*) was refluxed for 5 hr. A resulting white precipitate was filtered and recrystallized from the mixture of alcohol and ether giving triphenylisopropylphosphonium iodide, 4.18 g (99%), mp 195°C. The filtrate was evaporated *in vacuo* to give a white precipitate. After the neutralization with hydrochloric acid, an oily product was obtained. Distillation under reduced pressure gave *S*-ethyl α-butyrylthiobutyrate, 0.79 g (77%), bp 126—128°C/15 mmHg.

Preparation of Triphenyl-α-benzoylisopropylphosphonium Iodide. Benzoyl chloride (14.10 g, 0.10 mol) was added dropwise to the solution of isopropylidenetriphenylphosphorane, prepared from triphenylisopropylphosphonium iodide (43.20 g, 0.10 mol) and *n*-butyl lithium (0.10 mol) in tetrahydrofuran (200 m*l*) under nitrogen. The reaction mixture was refluxed for 5 hr under stirring. The resulting precipitate was filtered and was recrystallized from a mixture of alcohol and ether to give triphenyl-α-benzoylisopropylphosphonium iodide, 47 g (88%), mp 213—215°C.

Found: C, 62.13; H, 4.99%. Calcd for $C_{28}H_{26}IOP$: C, 62.69; H, 4.85%.

Reaction of Triphenyl-α-benzoylphosphonium Iodide with Sodium Ethylmercaptide. A mixture of triphenyl-α-benzoylisopropylphosphonium iodide (5.36 g, 0.01 mol) and sodium ethyl mercaptide (0.84 g, 0.01 mol) was refluxed in tetrahydrofuran for 5 hr under stirring. After removal of the solvent under reduced pressure, a small amount of ether was added to the residue. The precipitated crystals were filtered and the filtrate was distilled *in vacuo* to give 1-ethylthio-2-methyl-1-phenylpropene, 1.00 g (52%), bp 115—123°C/18 mmHg. The precipitate and the residue of the distillation were collected and were treated with aqueous 5% sodium hydroxide to give triphenylphosphine oxide, 2.06 g (74%), mp 153—154°C.

Reaction of Triphenyl-α-benzoylisopropylphosphonium Iodide with Potassium Cyanide. A mixture of triphenyl-α-benzoylisopropylphosphonium iodide (5.36 g, 0.01 mol) and potassium cyanide (0.66 g, 0.011 mol) in 10 m*l* of water and 10 m*l* of tetrahydrofuran was stirred at room temperature for 2 hr. The reaction mixture was extracted with 50 m*l* of ether. After the extract was evaporated under reduced pressure the residue was distilled *in vacuo* to give α-phenyl-β-methylcrotonitrile, 0.85 g (54%), bp 123—124°C/8 mmHg. The residue of the distillation was collected and was recrystallized from carbon tetrachloride to give triphenylphosphine oxide, 1.45 g (52%), mp 155—156°C.