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NEW METHODS FOR THE PREPARATION OF THIOVINYL ETHERS AND unsym-KETONES

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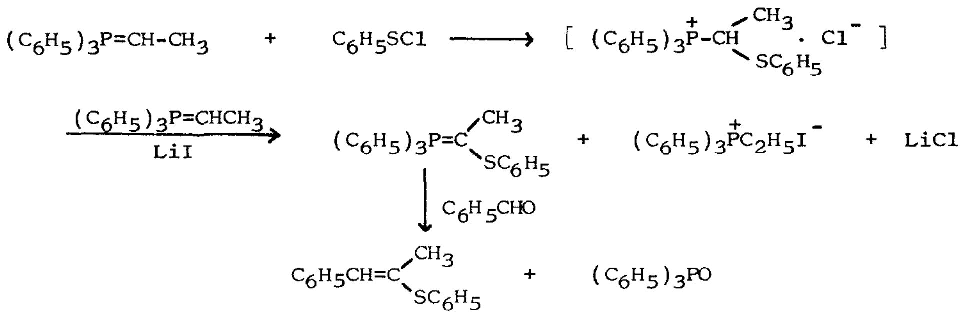
Authors wish to report a convenient method for the preparation of thiovinyl ethers from alkylidene phosphorane, benzenesulfenyl chloride, and carbonyl compounds. On the other hand, it has been known$^{1)}$ that thiovinyl ethers are hydrolyzed under acidic conditions to afford the corresponding ketones or aldehydes. Then a useful route to the syntheses of unsym-ketones and of aldehyde with the increased carbon atoms will be established.

It was found that thiovinyl ether derivatives were obtained in good yields by treating α-phenylmercaptoethylidenetriphenylphosphorane$^{1,2)}$, formed from ethylidenetriphenylphosphorane and benzenesulfenyl chloride, with aldehydes or ketones; for example, the reaction of 2 moles of ethylidenetriphenylphosphorane with 1 mole of benzenesulfenyl chloride in tetrahydrofuran at room temperature for 4 hours under nitrogen atmosphere and the subsequent reaction with benzaldehyde in refluxing tetrahydrofuran for 10 hours afforded 1-methyl-2-phenylvinyl phenyl sulfide and triphenylphosphine oxide in 79% and 65% yields, respectively, along with triphenylethylphosphonium iodide (quantative yield).

Benzyl methyl ketone was obtained in 73% yield as its 2,4-dinitrophenylhydrazone by refluxing the thiovinyl ether in 10% sulfuric acid and glacial acetic acid for 10 hours.



$$(C_6H_5)_3P{=}CH{-}CH_3 + C_6H_5SCl \longrightarrow [\,(C_6H_5)_3\overset{+}{P}{-}CH(CH_3)(SC_6H_5)\cdot Cl^-\,]$$

$$\xrightarrow[LiI]{(C_6H_5)_3P=CHCH_3} (C_6H_5)_3P{=}C(CH_3)(SC_6H_5) + (C_6H_5)_3\overset{+}{P}C_2H_5I^- + LiCl$$

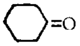
$$(C_6H_5)_3P{=}C(CH_3)(SC_6H_5) \xrightarrow{C_6H_5CHO} C_6H_5CH{=}C(CH_3)(SC_6H_5) + (C_6H_5)_3PO$$

The reaction of α-phenylmercaptoethylidenetriphenylphosphorane with butyraldehyde and benzophenone were also studied. The results are listed in Table I.

On n-butanesulfenyl chloride the same experiment was carried out. In this case resulted alkylmercaptoethylidenetriphenylphosphorane would be more reactive than the aromatic derivative toward carbonyl compounds owing to the increased nucleophilic character of the phosphorane. Actually the reaction of α(n-butylmercapto)ethylidenetriphenylphosphorane with ketones proceeds under milder conditions to give the expected thiovinyl ether derivatives comparing with those of the aromatic derivatives. These results are also shown in Table I:

TABLE I

Reaction of α-Phenylmercapto- or α(n-butylmercapto)ethylidenetriphenylphosphorane with Carbonyl Compounds

Carbonyl Compound	RSCl	Reaction Condition	Thiovinyl Ether Yield (%)	$(C_6H_5)_3PO$ Yield (%)	unsym-Ketone Yield (%)
C_6H_5CHO	C_6H_5SCl	THF Reflux 10 hr	79	65	73
$n\text{-}C_3H_7CHO$	C_6H_5SCl	THF Reflux 10 hr	73	99	19
$C_6H_5COC_6H_5$	C_6H_5SCl	Dioxane Reflux 10 hr	* —	—	—
C_6H_5CHO	$n\text{-}C_4H_9SCl$	THF Reflux 10 hr	56	55	80
$n\text{-}C_3H_7CHO$	$n\text{-}C_4H_9SCl$	THF Reflux 10 hr	71	82	47
	$n\text{-}C_4H_9SCl$	THF Reflux 10 hr	43	75	25

* In this reaction, benzophenone was recovered completely.

Further, it was found that n-butylmercaptomethylenetriphenylphosphorane was obtained by treating 1 mole of n-butanesulfenyl chloride with 2 moles of methylenetriphenylphosphorane. The phosphorane reacted with aldehydes and ketones to give the corresponding thiovinyl ethers in good yields. Various aldehydes were produced by the hydrolyses of the thiovinyl ethers. These results are listed in Table II.

$$(C_6H_5)_3P{=}CH_2 \quad + \quad n\text{-}C_4H_9SCl \longrightarrow [\,(C_6H_5)_3\overset{+}{P}\text{-}CH_2\text{-}SC_4H_9\text{-}n \cdot Cl^-\,]$$

$$\xrightarrow[LiI]{(C_6H_5)_3P=CH_2} [\,(C_6H_5)_3P{=}CH\text{-}SC_4H_9\text{-}n\,] \quad + \quad (C_6H_5)_3\overset{+}{P}CH_3\overset{-}{I}$$

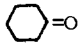
$$\Big\downarrow C_6H_5CHO$$

$$C_6H_5CH{=}CHSC_4H_9\text{-}n \quad + \quad (C_6H_5)_3PO$$

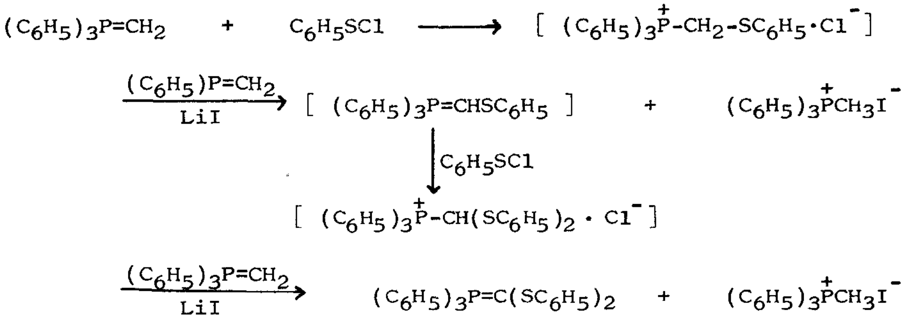
$$C_6H_5CH{=}CHSC_4H_9\text{-}n \xrightarrow{H^+} C_6H_5CH_2CHO \quad + \quad n\text{-}C_4H_9SH$$

TABLE II

Reaction of n-Butylmercaptomethylenetriphenylphosphorane with Carbonyl Compounds

Carbonyl Compound	Reaction Condition	Thiovinyl Ether Yield (%)	$(C_6H_5)_3PO$ Yield (%)	Aldehyde Yield (%)
C_6H_5CHO	THF Reflux 10 hr	77	49	49
$n\text{-}C_3H_7CHO$	THF Reflux 10 hr	75	70	20
	THF Reflux 10 hr	65	73	78

On the other hand, in the case of benzenesulfenyl chloride, diphenylmercaptomethylenetriphenylphosphorane (70%) and methyltriphenylphosphonium iodide (quantitative yield) were obtained by treating 3 moles of methylenetriphenylphosphorane with 2 moles of benzenesulfenyl chloride at room temperature for 10 hours under nitrogen. Diphenylmercaptomethylenetriphenylphosphorane, a yellow crystalline compound, m.p. 164-5°, did not react further with benzaldehyde at all even after refluxing in dioxane for 10 hours.



$$(C_6H_5)_3P{=}CH_2 + C_6H_5SCl \longrightarrow [\,(C_6H_5)_3\overset{+}{P}{-}CH_2{-}SC_6H_5\cdot Cl^-\,]$$

$$\xrightarrow[LiI]{(C_6H_5)P=CH_2} [\,(C_6H_5)_3P{=}CHSC_6H_5\,] + (C_6H_5)_3\overset{+}{P}CH_3I^-$$

$$\big\downarrow C_6H_5SCl$$

$$[\,(C_6H_5)_3\overset{+}{P}{-}CH(SC_6H_5)_2\cdot Cl^-\,]$$

$$\xrightarrow[LiI]{(C_6H_5)_3P=CH_2} (C_6H_5)_3P{=}C(SC_6H_5)_2 + (C_6H_5)_3\overset{+}{P}CH_3I^-$$

In conclusion, it can be noted that unsym-ketone and an aldehyde with the increased number of carbon atoms are conveniently synthesized from a carbonyl compound and an alkyl halide via two intermediates, i.e. a mercaptoalkylidene-triphenylphosphorane and a thiovinyl ether.

REFERENCES

1) G. Wittig and M. Schlosser, Chem. Ber., 94, 1373 (1961)

2) H. J. Bestmann and B. Arnason, Chem. Ber., 95, 1513 (1962)