The Production of New Carbonyl- and Thiocarbonyl-stabilized Phosphonium Ylids by the Reaction of the Triphenylphosphonium Methylid with *O*-Alkylxanthates

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The reaction of phosphonium alkylids with *S*-alkyl thiolcarboxylates yields phosphonium acylalkylids in good yields.[1] However, no worker has reported on the reaction of dialkylcarbonates with phosphonium alkylids. In this communication, the reaction of triphenylphosphonium methylid (**1**) with *O*-alkylxanthates (**2**) to give new carbonyl- and thiocarbonyl-stabilized phosphonium ylids will be treated.

The reaction of **1** with a two fold amount of **2** was performed in toluene under a nitrogen atmosphere at various temperatures. The product was then purified by recrystallization from petroleum ether-ethyl acetate or by column chromatography. The structure of the product was confirmed by elemental analysis, NMR, IR and a Wittig reaction with benzaldehyde.

As Table 1 shows, the reaction at room temperature yields only thiocarboalkoxymethylene triphenylphosphorane (**3**); however, the reaction at 130°C yields **3** or **4**, or a mixture of the two. The alkyl groups attached to the ylids, **3** and **4**, are the *O*-alkyl groups of the starting xanthates, **2**.

Table 1. The reaction of **1** with **2** in toluene

2		Reaction condition		Yield (%)	
R	R′	Temp. (°C)	hr	**3**(R)[a]	**4**(R)[a]
Me	Me	room temp.	24	38	—
		130	3.5	—	46
Me	Et	130	3	—	47
Et	Me	room temp.	24	41	—
		130	3	53[b]	
Et	Et	130	3	59[b]	
i-Pr	Me	130	3	56	—

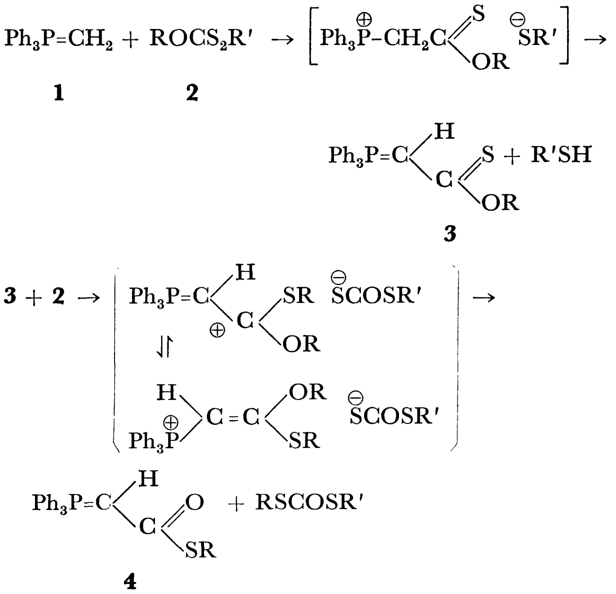
a) The same group as the *O*-alkyl R of the xanthate **2**.
b) Nearly equimolar mixture of **3** and **4**.

Mps: **3** (R=Me) 164—165.5, **3** (R=Et) 137—139, **3** (R=*i*-Pr) 155—156.5, **4** (R=Me) 220—221, **4** (R=Et) 177—182°C.

The formation of **4** did not result from a intramolecular thion-thiol rearrangement of **3** similar to the Schönberg rearrangement,[2] since **3** (R=Me, Et, *i*-Pr) remained unchanged on heating at 130°C for a few hours. On the other hand, reaction **3** (R=Et) with **2** (R=R′=Me) gave, almost quantitatively, **4** (R=Me) and methyl ethyl dithiolcarbonate.

It is known that carboalkoxy ylids undergo alkylation with a variety of alkyl halides to afford normal alkylated ylids (alkylation on carbanion);[3] however, alkylation with triethyloxonium fluoroborate does not yield normal alkylation products (alkylation on carbonyl oxygen).[4] The alkylation of **3** with methyl and ethyl iodides yields exclusively an *S*-alkylated product.[5] Thus, the formation of **4** may be from the alkylation of **2** to the highly-polarized thiocarbonyl sulfur of **3**. The present authors have previously reported that **2** reacts with tertiary amines as an alkylating reagent and that the reactivity decreases in the order: Me≫Et>*n*-Pr≫*i*-Pr.[6] This order agrees well with that of the yield of **4** at 130°C (Table 1). Thus, the reaction of **1** with **2** to give **3** and/or **4** may be pictured as follows:

The physical and chemical properties of **3** and other analogs will be published later.



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