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Reactions of Stable Wittig Reagents with Episulfides

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Stable Wittig reagents effectively reacted with episulfides to afford dialkyl fumarates and dialkyl maleates in good yields. The reaction probably occurred via attack of the ylide carbanion on episulfide's sulfur to form a thiocarbonyl intermediate. The ylide further attacked this thiocarbonyl intermediate to give the final olefins.

The Wittig reaction has been widely adopted for the synthesis of olefins.[1)] In the past decades, several authors have reported the reaction of Wittig type reagents with epoxides to afford cyclopropane derivatives.[2)] Recently, Corey et al. showed that the reaction of phosphonium ylide dianions with epoxides, followed by the addition of carbonyl compounds gave γ-hydroxy olefin derivatives.[3)] But there is no report on the reaction of these ylides with episulfides (**1**). In this communication, we would like to report the reactions of stable phosphonium ylides (**2**) with **1** to give olefins.

A typical synthetic procedure was as follows: To a solution of styrene sulfide (**1a**) (1.36 g, 10 mmol) in toluene (30 ml) was added a solution of triphenylcarbomethoxymethylenephosphorane (**2a**) (3.34 g, 10 mmol) in toluene (30 ml). After refluxing for three days, the reaction mixture was evaporated and extracted three times with hexane. The combined extracts were evaporated and distilled to give styrene (**4**) (0.42 g) and the corresponding olefins (**5**) (0.56 g) in 42% and 77% yields, respectively. Other reactions were carried out in a similar manner.

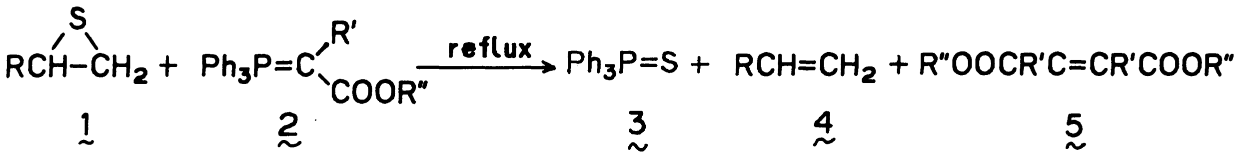
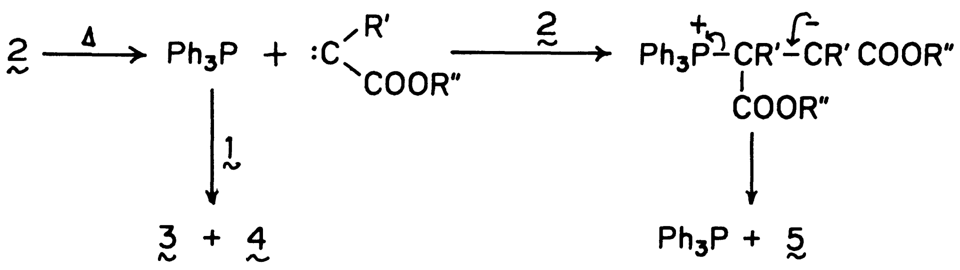


Table 1. Reaction of 1 with 2

1		2			Conditions		Products yield/%[4]			
	R		R'	R"	solvent	time/d	3	4	5	trans/cis
a	Ph	a	H	Me	toluene	2	85	42	77	14.4
a	Ph	a	H	Me	benzene	8	48	22	35	16.5
b	Me	a	H	Me	toluene	8	12	-	6	12.0[a]
c	Et	a	H	Me	toluene	8	35	-	12	14.0[a]
a	Ph	b	H	Et	toluene	2	84	40	70	3.1
a	Ph	c	H	i-Pr	toluene	2	88	45	82	4.8
a	Ph	d	Me	Me	toluene	2	85	43	56	1.8
a	Ph	e	Me	Et	toluene	2	85	42	54	2.0

a) Starting 2a was recovered in 75% and 55% yields, respectively.

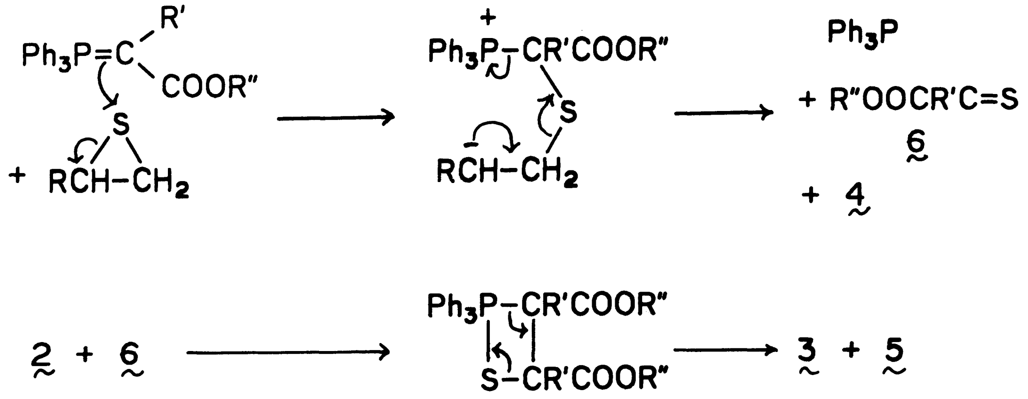
Phenylmethylenetriphenylphosphorane was thermally decomposed over 240 °C to give symmetrical olefins via carbene intermediates.[5] In our case, the reaction might proceed through similar carbene intermediates as shown in Scheme 1.



Scheme 1.

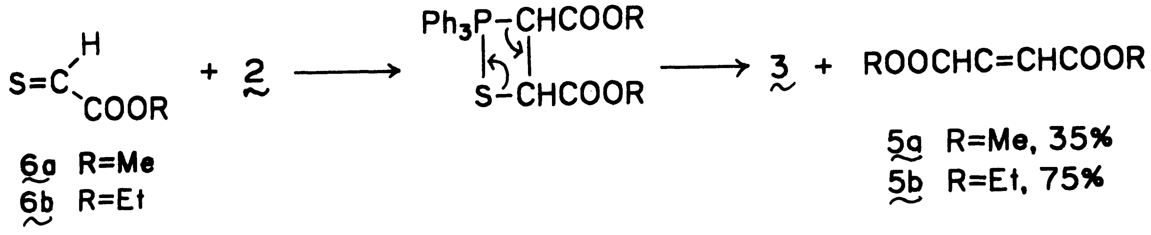
To confirm the above mechanism, the reaction of 2 in refluxing toluene was carried out. Thermolysis of 2a and 2b without 1 in toluene did not afford the olefins but only the recovered starting materials even after refluxing for 8 d. This result showed that the above mechanism was not correct.

Phosphonium ylides have been found to react with sulfur. Staudinger and Meyer reported the cleavage of benzhydrylidenetriphenylphosphorane in the presence of sulfur gave thiobenzophenone and triphenylphosphine sulfide.[6] Similarly, Schönberg et al. found that fluorenylidenetriphenylphosphorene cleaved in the presence of sulfur to thiofluorenone.[7] Tokunaga and coworkers also reported that the reaction of sulfur with diarylmethylenetriphenylphosphoranes gave the corresponding thioketones in good isolated yields.[8] These cleavages probably occurred via attack of the ylide carbanion on sulfur to form a zwitterionic intermediate. The reaction of stable Wittig reagents with episulfides can also be rationalized by the following zwitterionic mechanism (Scheme 2).



Scheme 2.

The ylide carbanion attacks episulfide sulfur to give the corresponding thioaldehyde (6). The resulting 6 further reacts with phosphonium ylide to afford olefin via a Wittig-like reaction. Recently, Kirby and coworkers reported the generation of 6 by the reaction of ethoxycarboxymethanesulfenyl chloride with triethylamine.[9] To confirm the above mechanism, we tried the reaction of 6 with 2. As shown in Scheme 3, corresponding olefins were obtained in good yields.



Scheme 3.

This is the first example of the reaction of Wittig reagent with thioaldehyde.

Our reaction is quite different from those of 2 with epoxides. In the case of epoxides, the products were cyclopropane derivatives or ring-opened alcohols.[2,3] On the other hand, symmetrical olefins were obtained by using episulfides. The above observations were explained by the electronegativity difference of sulfur and oxygen. In the case of epoxides, the ylide carbanion attacks the epoxide carbon to give a five-membered intermediate.10) On the other hand, the episulfide sulfur was attacked initially by the ylide carbanion because episulfie carbons are not so positive as epoxide carbons.

In summary, when stable Wittig reagents were allowed to react with episulfides, dialkyl fumarates and dialkyl maleates were obtained in good yields. The reaction might proceed via thiocarbonyl intermediate. We also found the Wittig-like reaction of **2** with thioaldehyde to give olefins in moderate yields.

We are now continuing synthetic studies of **2** with episulfides and thio carbonyl compounds.

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