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REACTIONS OF OXOSULFONIUM YLIDES WITH KETENES. THE FORMATION OF ENOL-LACTONES AND DIHYDROFURANONES[1]

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The reaction of diphenyloxosulfonium p-methoxyphenacylide with dialkyl- or alkylaryl-ketenes gave enol-lactones in good yields, whereas the reaction of diphenyloxosulfonium phenacylide with diarylketenes led to dihydrofuranones besides the enol-lactones.

Many studies have been carried out on the reaction of stable sulfonium ylides with carbonyl compounds,[2,3] but only a few papers were published on the reaction with ketenes. Payne[4] observed that the reaction of a sulfonium ylide stabilized by ethoxycarbonyl substituent with diphenylketene gave a sulfonium ylide which was composed of one molecule of the ylide and two molecules of the ketene. This paper deals with the reaction of diphenyloxosulfonium phenacylides[5] with dialkyl-, alkylaryl-, or diarylketenes.

A benzene solution of an oxosulfonium phenacylide (I, 3 mmol) and a disubstituted ketene (II, 10 mmol) was refluxed for five hours and the reaction products were separated by means of silica gel column chromatography. In the reaction of diphenyloxosulfonium p-methoxyphenacylide (I_A; X=H, Y=OCH_3) with disubstituted ketenes, γ-enol-lactones (III) were produced together with diphenyl sulfoxide (V), regardless of the substituent in the ketenes. Similar results were obtained in the reaction of p,p′-dichlorodiphenyloxosulfonium phenacylide (I_B; X=Cl, Y=H) with dialkyl- or alkylaryl-ketenes, whereas dihydrofuranones (IV) were formed in addition to the corresponding enol-lactones (III) and sulfoxide (V) in the reaction with diarylketenes (see Table 1).

The ir spectra of all enol-lactones (III) obtained showed absorption bands near 1780 (lactone C=O) and 1650 cm^{-1} (C=C), and their nmr spectra exhibited a proton signal near 4.10 τ (s, 1H, -CH=C) besides those of OCH_3, C_2H_5, and aryl groups. On the contrary, the dihydrofuranones (IV) obtained showed an absorption band at 1690 cm^{-1} (cyclic C=O) without any lactone carbonyl bands, and a proton signal at 3.90 τ (s, 1H, -CH=C).

It has been pointed out that sulfonium ylides with carbonyl substituent on the ylide carbon are stabilized owing to large contribution of the betaine structure besides the ylene structure.[6] Because of the large resonance contribution of (I′) in ylide I_A (Y=OCH_3), nucleophilicity of carbonyl oxygen of the ylide increased. Consequently, a nucleophilic attack of the carbonyl oxygen of I_A on the carbonyl carbon of ketenes should occur preferentially to give enol-lactones (III) via intermediate (VI) in the reaction of ylide I_A (path a).[7] However, in the reaction of diarylketenes with

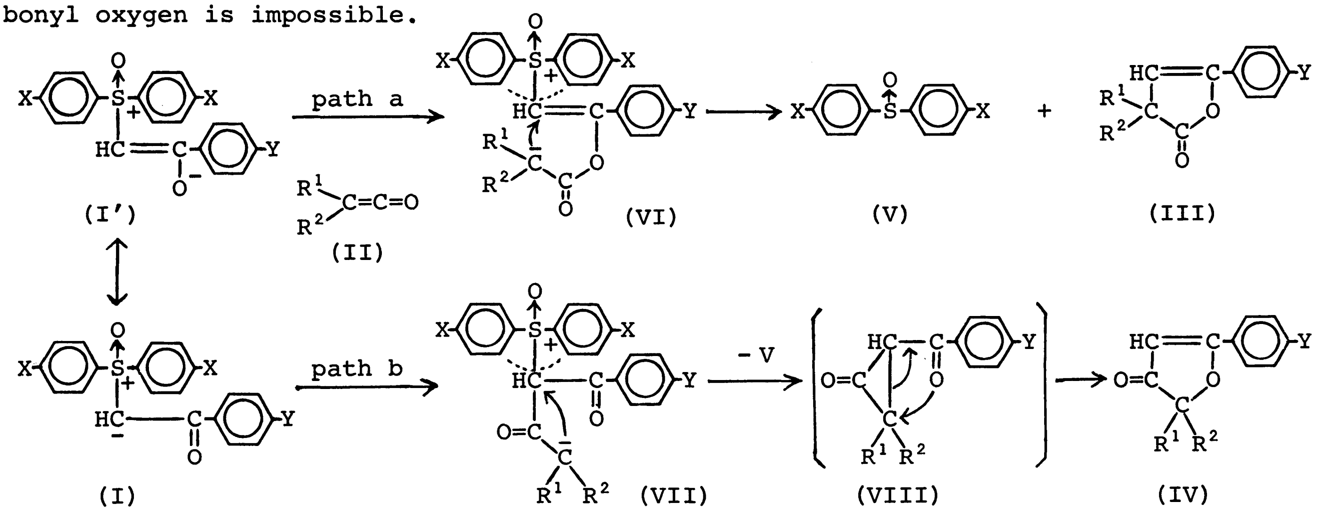
TABLE 1. Yields and Melting Points of Reaction Products

Run	I		II		III		IV		V
	X	Y	R^1	R^2	yield (%)	mp (°C)	yield (%)	mp (°C)	yield (%)
a	H	MeO	Et	Et	98	60	-		94
b	H	MeO	Et	Ph	95	91	-		83
c	H	MeO	Ph	Ph	90	171	-		80
d	H	MeO	Ph	Mesityl	72	150	-		80
e	Cl	H	Et	Et	93	33	-		98
f	Cl	H	Et	Ph	80	101	-		82
g	Cl	H	Ph	Ph	80	120	10	176	80
h	Cl	H	Ph	Mesityl	44	162	42	172	81

The reaction products showed satisfactory elemental analyses.

ylide I_B (Y=H), in which contribution of the resonance structure I′ is not so large, nucleophilic attack of the ylide carbon on the carbonyl carbon of ketene also takes place affording dihydrofuranones (IV) via intermediate VII (path b). The leaving facility of diphenyl sulfoxide in the intermediates VI and VII forms III and IV by intramolecular nucleophilic substitution, and not by the intermolecular attack on the second molecule of ketene as observed by Payne.[4]

A tentative mechanism involving an intermediate (VIII) is shown below for the formation of IV from VII, because direct attack of the anionic carbon in VII on the carbonyl oxygen is impossible.



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