

EFFECTS OF STRONG π -ELECTRON ACCEPTING SUBSTITUENTS
 ON STRUCTURE PREFERENCE FOR THIOCARBONYL YLIDE OR THIIRANE

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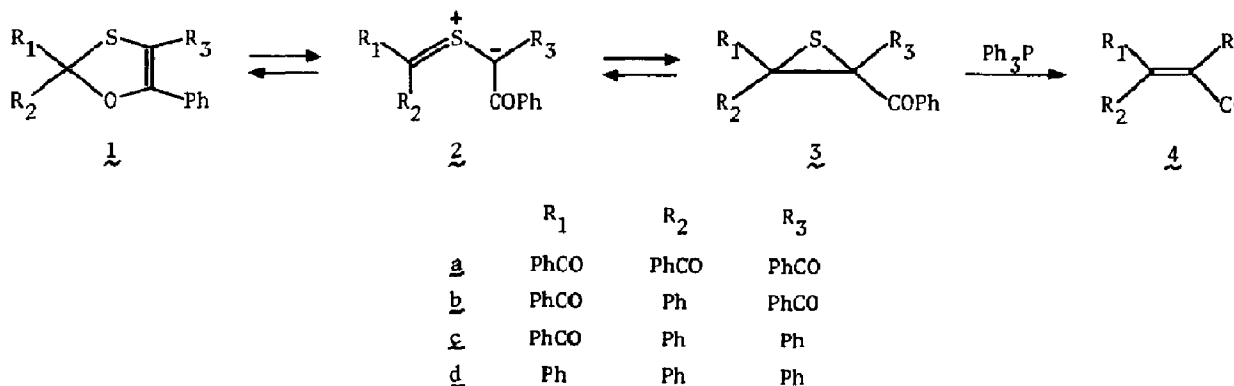
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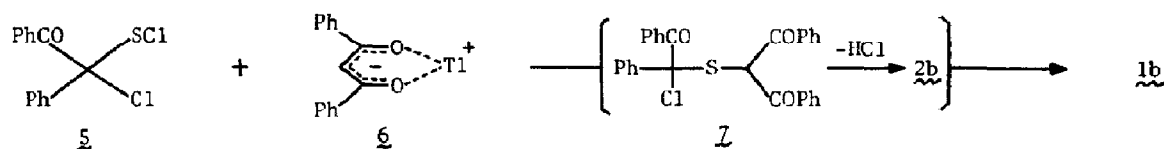
Summary: Equilibrium between thiocarbonyl ylide and thiirane depends upon the π -electron accepting nature of the substituents. Four carbonyl and ester groups move the equilibrium far to the thiocarbonyl ylide side.

Thiocarbonyl ylide and thiirane may exist in an equilibrium operating via a conrotatory 4 electrocyclic reaction.¹ The equilibrium of the substituent unperturbed systems lies far on the thiirane side,¹ while in the perturbed "push-pull" substituted systems the ylide is favored owing to effective charge delocalization.^{2,3} In the present paper, we wish to report a new synthetic approach to the "pull-pull" substituted systems and their distinct chemical characters.

After the first synthesis of dibenzoyldiphenylthiirane 3c by Dittmer⁴ and photochemical investigations by Padwa,⁵ Norin⁶ reexamined this problem and has determined the correct structure to be an oxathiole 1c. The known conversion of 1c to dibenzoylstilbene 4c demonstrated the equilibrium of 1c with 3c.^{5,6} An intermediate of this equilibrium may be the thiocarbonyl ylide 2. However, efforts to confirm this intermediacy were not successful⁷ in spite of an expectation that the ylide should be stabilized by two strong π -electron accepting substituents which, in turn, destabilize the thiirane by weakening the C-C bond. These considerations compelled us to synthesize the other congeners substituted with different numbers of π -electron accepting groups to ascertain their relative thermodynamic stabilities.

The analogue 1a was prepared from dibenzoylmethane by the action of thionyl chloride.⁸ Oxathiole 1b (mp 140-142°C) was prepared from sulfonyl chloride 5⁹ by treatment with thallium(I) dibenzoylmethanate 6 (mp 164-166°C (dec)). A possible intermediate of this reaction may be a sulfide 7 which then undergoes dehydrochlorination to give the ylide 2b. Preparation of 1d has been reported recently.¹⁰



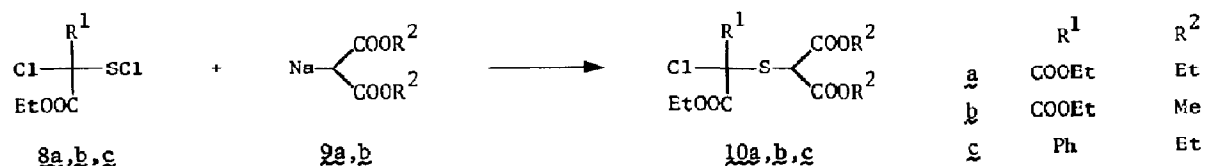
Table 1. Characteristic mass spectra of 1,3-oxathioles 1a-d.

Compound	Number of PhCO group	Base Peak	Intensity %		$(M^+ - S)/M^+$
			M^+	$M^+ - S$	
<u>1a</u>	4	$M^+ - \text{PhCO}$	33	1.2	0.036
<u>1b</u>	3	$M^+ - \text{PhCO}$	1.6	4.3	2.69
<u>1c</u>	2	$M^+ - \text{PhCO}$	0.45	0.38	0.84
<u>1d</u>	1	$M^+ - S$	41	100	2.44

We have compared the fragmentation pattern of the four compounds 1a-d. If there were a gas phase ylide-thiirane conversion favoring the latter, a relatively strong $M^+ - S$ peak should be observed and the ratio of intensities $(M^+ - S)/M^+$ may reflect the extent of the reaction $1 \rightarrow 2 \rightarrow 3$. Tetrabenzoyl congener 1a exhibited a very weak $M^+ - S$ peak as shown in Table 1. On the contrary, 1b-d exhibited a strong $M^+ - S$ peak which suggested that the conversions to thiiranes would be favored. The same structure preference was further observed in solution by chemical methods: rate of desulfurization of the oxathioles in refluxing xylene containing triphenylphosphine. The reaction time necessary for complete desulfurization increased with increasing numbers of the benzoyl substituents (1b, 30 hr; 1c, 24 hr; 1d, 20 hr). The tetrabenzoyl congener 1a remained completely intact under these reaction conditions for a period of 72 hours.

In the above mentioned experiments, the ylides underwent facile 6π -electrocyclization giving the thermodynamically favored oxathioles, so as to move the equilibrium far from the thiirane side. Consequently, we decided to synthesize another series of compounds containing ester group as the π -electron accepting substituents. The requisite chlorosulfides 10 were prepared from sulfonyl chlorides 8^{9,11} by treatment with the sodium salt of malonates 9.

The tetraethoxycarbonyl sulfide 10a was treated with 1.2 molar equivalents of *t*-BuOK in THF at -78°C . The solution changed to an orange-red color which then disappeared at -30°C . This unstable colored material was assumed to be the ylide 11a. The crude products showed a single spot on TLC and direct recrystallization from isopropyl ether gave the olefin 12a in pure form. However, the NMR clearly showed the plural components. Thus we used HPLC with silica gel to obtain the olefin 12a, 1,3-dithietan 13a, and 1,2,4-trithiolan 14a in 55, 5, and 20% yields, respectively. The yields of 13a and 14a depended upon the amounts of the reagent used: slightly less amounts of the reagent minimized the yield of 14a and maximized that of 13a. The increase of 12a was in accordance with the increase of 14a indicating that the formation of 14a took place



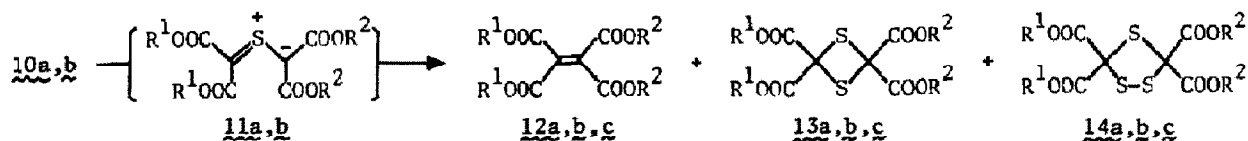
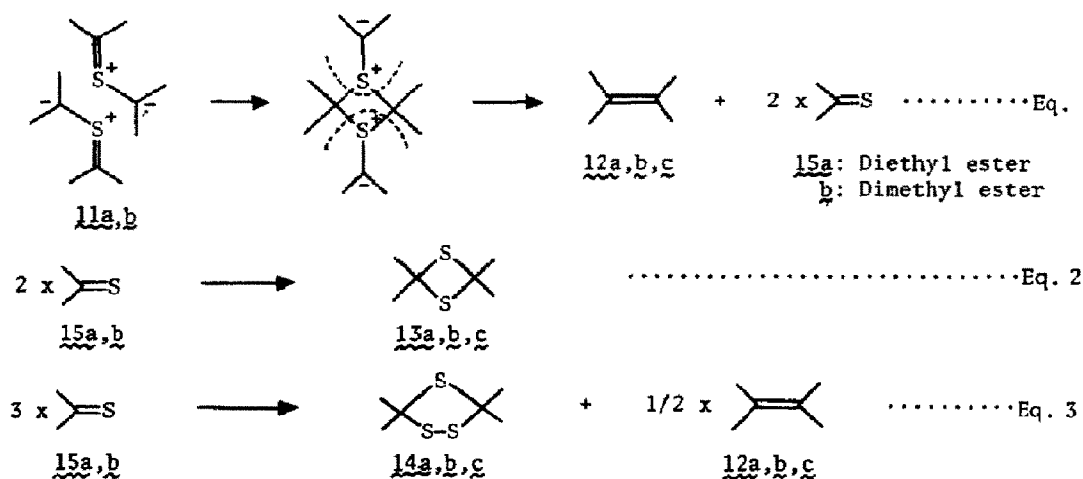


Table 2. Product distribution of cross-over reaction of thiocarbonyl ylide 11b. (Total yield of the reaction: 85%, 496 mg; recovery of HPLC: 88%)

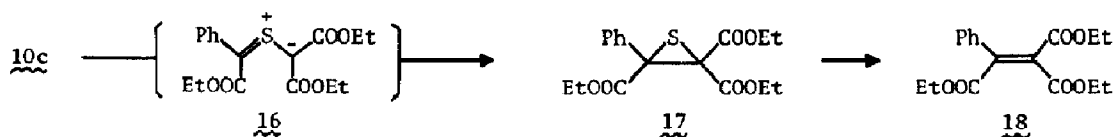
Compound	Elution order	Yield		mp (°C)		R ¹	R ²
		mg	mmol				
<u>12a</u>	1	32	0.101	56-57 (lit. 55-57) ¹⁴		Et	Et
<u>12b</u>	4	122	0.424	20		Et	Me
<u>12c</u>	7	75	0.288	119-120		Me	Me
<u>13a</u>	2	67	0.176	51-52 (lit. 51-51.5) ¹¹			
<u>13b</u>	6	68	0.193	oil			
<u>14a</u>	3	19	0.046	61-62			
<u>14b</u>	5	3	0.008	—			
<u>13c</u> + <u>14c</u>	8	50	0.14	—			
Total		436	1.376				

Scheme 1



through the thione-trimerization (Scheme 1, Eq.3).¹² Production of 13a via the thione-dimerization (Scheme 1, Eq.2) was well demonstrated.¹³ These considerations indicated that the olefin 12a and thione 15a have to be produced in the initial step via the [$\pi 2s + \pi 2a$] cycloaddition reaction of the thiocarbonyl ylide 11a (Scheme 1, Eq.1) which has close analogy with the observed ligand exchange reaction of the "push-pull" substituted systems.²

To obtain more detailed information, we decided to perform a cross-over experiment using asymmetrically substituted chlorosulfide 10b. In this case, the products were separated into eight fractions by HPLC using silica gel. The structures of these compounds were assigned as summarized in Table 2. It has been clearly shown that the reaction proceeded intermolecularly and the distribution of the olefins (12a:12b:12c = 0.101:0.424:0.288) may be understandable in



terms of the conditional probabilities of the molecular combinations owing to their regioselectivities which may be more favorable to the methyl-side anion as the π -electron donor than the ethyl-side anion.

The next object of our study is the structure preference for ylide or thirane when the congener contains three ethoxycarbonyl groups. In the case of the compound 10c, the product obtained in quantitative yield was assigned as the thirane 17 which was desulfurized to give olefin 18 quantitatively. Another congener which contains two ethoxycarbonyl groups has not been examined. However, the reported experiments¹³ on synthesizing olefin from ethyl phenylacetate the action of thionyl chloride revealed the same structure preference.

It is worth mentioning that the reported synthesis¹³ giving a good yield (85-90%) of the olefin 12a from diethyl malonate under the action of thionyl chloride seems to be mechanistically similar to the present ligand exchange reaction. We repeated the reaction and have isolated olefin 12a together with the sulfur-containing products 13a and 14a in fairly good yields.

In conclusion, we would like to propose that the very strong π -electron accepting substituents, four carbonyl or ester groups, on thiranes weaken their C-C bond and move the equilibrium far to the ylide side. The results make clear the scope and limitation of our synthetic sequence for olefins via "pull-pull" substituted thiocarbonyl ylides and/or thiranes as the intermediate.

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