

**HOMOLOGATION OF ALDEHYDES USING
(PHENYLTHIOMETHYLENE) TRIPHENYLARSORANE : SELECTIVE PREPARATION
OF α -THIOPHENOXYEPOXIDES AND PHENYLTHIOENOL ETHERS**

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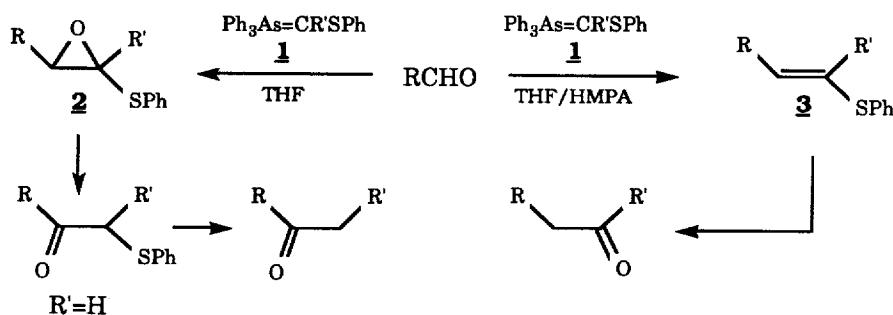
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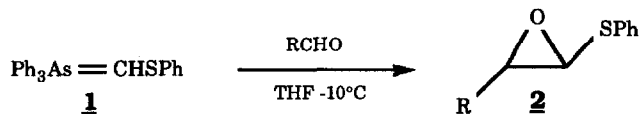
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

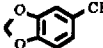
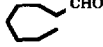
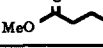
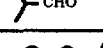
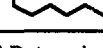
Summary : The title arsonium ylide reacts with aldehydes to give exclusively α -thiophenoxyepoxides in THF and phenylthioenol ethers in THF/HMPA. The former adducts are readily transformed to α -thiophenoxy carbonyls and the latter to one-carbon homologated aldehydes.

Arsonium ylides emerged in recent years as useful reagents for organic synthesis¹. Addition of unstabilized ylides to carbonyls leads specifically to E-epoxides² whereas stabilized ylides afford only olefins³. Semi-stabilized, e.g., allylic and benzylic ylides display a dual reactivity dependent upon structure and reaction conditions⁴. However, relatively little is known about the mechanistic consequences of heteroatom substitution at the ylide carbon and its influence on product distribution⁵. Herein, we describe the preparation of (phenylthiomethylene) triphenylarsorane (**1** R'=H) and its utility for the homologation of aldehydes via the selective synthesis of α -thiophenoxy epoxides **2** and phenylthioenol ethers **3**.



Reaction of several representative aldehydes with ylide **1** in THF^{4a,b} at -10°C (procedure A) affords α -thiophenoxyepoxides **2** in good yield⁶ (Table I). In contrast to the usual course of the epoxide formation by arsonium ylides^{2,4d,5}, the Z-isomer, arising from the corresponding *threo*-betaine, predominates in each case. Previously, α -thiophenoxy epoxides have been prepared directly from carbonyls using sulfonium ylides or chloromethyl aryl sulfide in the presence of potassium *tert*-butoxide⁷. The present method, by comparison, is generally superior with regard to ease of operation and yield.

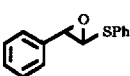
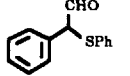
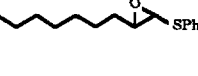
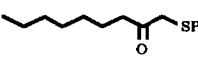
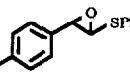
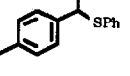
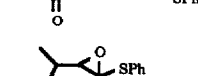
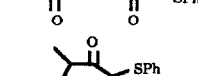
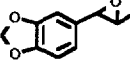
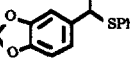


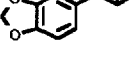
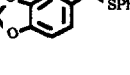
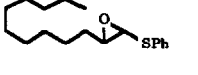
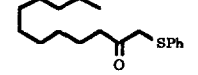
Table I. Reaction of ylide **1** with aldehydes in THF.

Aldehyde	2/3	E / Z ^a	Yield (%)
	100/0	20/80	70
	100/0	10/90	85
	100/0	15/95	80
	100/0	20/80	90
	100/0	30/70	75
	100/0	25/75	70
	100/0	25/75	85

^a Determined by ¹H NMR

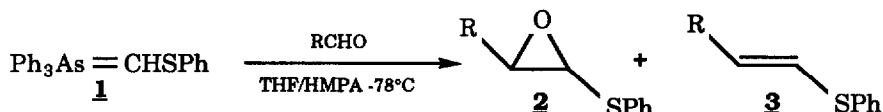
Brief exposure of **2** to silica gel results in quantitative rearrangement to α -thiophenoxy carbonyls (Table II) which are themselves useful synthetic intermediates⁸. The type of rearrangement is dictated by the nature of the adduct⁷. Those from aromatic aldehydes give rise to α -thiophenoxy aldehydes by migration of the aryl (or thiophenyl) group. Preferential hydrogen migration to α' -thiophenoxy ketones is observed with adducts from aliphatic aldehydes. Desulfuration leads to the corresponding methyl alkyl ketones.

Table II. Rearrangement

Aryl-epoxides		Alkyl-epoxides	
Epoxisulfide	Rearranged product	Epoxisulfide	Rearranged product
			
			
			
			

Condensations using ylide **1** in THF/HMPA at -78°C (procedure B) are dramatically different^{4a,b}. Aromatic aldehydes yield E-phenylthioenol ethers **3** exclusively⁸ (Table III). The union with aliphatic partners is less stereoselective, but still favors the E-isomer, and is accompanied by small amounts of **2**. Again, the major pathway to products is through the *threo* betaine. Since thioenol ethers such as **3** are readily transformed into aldehydes¹⁰ or functionalized aldehydes¹¹ under mild conditions, Procedure B formally represents a one-carbon homologation of aldehydes.

Table III. Reaction of ylide **1** with aldehydes in THF/HMPA.



Aldehyde	2/3	2 E / Z ^a	3 E / Z ^a	Yield ^b (%)
	0/100	—	100/0	67
	0/100	—	100/0	63
	0/100	—	100/0	55
	10/90	25/75	95/5	70
	10/90	25/75	70/30	65
	10/90	30/70	95/5	69
	10/90	35/65	60/40	76

^a Determined by $^1\text{H NMR}$. ^b Combined yield of **2** and **3** (isolated yields)

Arsonium Salt Preparation:

Equimolar amounts of triphenylarsine, sodium iodide and chloromethyl phenyl sulfide are heated at reflux in acetonitrile (10 mmol each/15 ml) for 3h, cooled to ambient temperature, filtered, and the solvent removed in vacuo. Trituration of the residue under ether furnishes the arsonium iodide as a stable, light yellow powder (54%), mp 112°C (dec).

Procedure A:

To a stirred suspension of arsonium salt (1mmol) in 10 ml of THF under argon at -30°C is added n-butyllithium (1.1 mmol, 1.6 M in hexane). After 30 min, the dark yellow, homogeneous solution of **1** is warmed to -10°C and the aldehyde (1 mmol) is added dropwise. The mixture is

allowed to come to room temperature over 3h, quenched with water, and extracted with ether (3 x 20 ml). The combined ethereal extracts are washed with brine, dried over sodium sulfate, and concentrated in vacuo. Flash chromatography over triethylamine-deactivated silica gel affords **2**.

Procedure B:

Generation of the ylide **1** according to procedure A in THF/HMPA (85:15) gives a red, homogeneous solution to which the aldehyde is added at -78°C. Extractive isolation and chromatography as above provides **3** as well as a small amount of **2**, if the aldehyde is aliphatic.

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