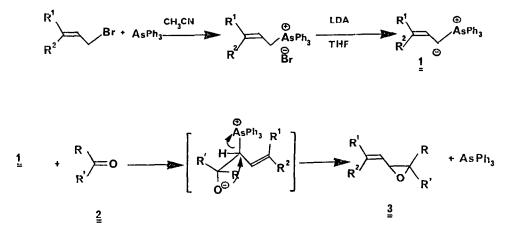
SYNTHESIS OF VINYLIC EPOXIDES VIA ARSONIUM YLIDES

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Abstract. Vinylic epoxides were synthesized in high yields from allylic arsonium ylides and carbonyl compounds.

Recently Still¹ demonstrated the synthetic utility of nonstabilized arsonium ylides by performing a highly stereoselective synthesis of trans-epoxides. It is also known that stabilized ylides react with carbonyles to give alkenes like phosphonium ylides². In this communication we report that allylic arsonium ylides react cleanly with aldehydes and ketones to give vinylic epoxides with the highest yields ever reported for direct epoxidation of carbonyl compounds (scheme 1).



Scheme: I

Vinylic epoxides cannot be prepared in a suitable way from allylic dimethylsulfonium ylides which undergo |2,3| sigmatropic rearrangements³ nor from allylic diphenyl sulfonium ylides which are difficult to prepare⁴. In sharp contrast, triphenylarsine, being more nucleophilic than diphenyl sulfide, reacts nicely with allylic bromides to give the corresponding allylic arsonium salt and therefore the corresponding allylic arsonium ylide⁵.

In a preceeding paper⁶ we have shown that semistabilized arsonium ylides give selectively epoxides if the right solvent system is used. As shown in Table I, allylic arsonium ylides react in THF with carbonyles to give high yields of the corresponding vinylic epoxides.

In a typical experiment ylide $\underline{1}$ (R' = R² = H) was prepared by adding 1.1 equiv. of LDA (Lithium di-isopropylamide) to the corresponding arsonium salt⁵ in THF at -40°C (1 hour). Then 0.8 equiv. of α -naphtaldehyde was added at -78°C and the reaction mixture allowed to warm slowly to room temperature.

Aqueous work-up, followed by chromatography on silicagel impregnated with triethylamine, gives a mixture of cis and trans epoxides⁷. Triphenyl arsine can be recycled or removed before chromatography by oxidation with neutral H_2O_2 in DME/ H_2O (1:1) at room temperature when the chromatographic separation is difficult.

The survey of the results presented in Table 1 shows that the scope of this reaction is quite broad : aliphatic and aromatic aldehydes and ketones as well as α,β -unsaturated aldehydes give good yields of the corresponding vinylic epoxides.

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TABLE I

TABLE I				
	Carbonyl Compound <u>2</u>	Ylide <u>1</u>	Epoxide <u>3</u> (cis + trans)	Yield % ^(b)
1	CHO COO	AsPh3		65
2	CHO CHO			55
3	<00 сно		~10 ^Å)	76
4	~~~сно		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	65
5	\sim		↓	70
6	Cr(CO)3	AsPh3	Cr(CO)3	55
7	<°=⊂O [−] CH°		\$IO]	90
8	4		+~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	95
9	∕∼сно			85
10	CH0 CH0			83
11	сно	AsPh3	~~^^(c)	75
12		\checkmark	JÅ O ^(c)	81
13	Cr(CO)3			57
14	+~~~~°			75

- a) benzene was used as solvent and butyraldehyde added at 5°C.
 - b) Yields based on carbonyl compound $\underline{2}$.
 - c) from ref. 6.

- 4) a) R.W. La Rochelle, B.M. Trost and L. Krepski, J. Org. Chem. <u>36</u>, 1126 (1971)
 b) J.P. Beny, J.C. Pommelet and J. Chuche, Bull. Soc. Chim. France II-369 (1981)
 c) B.M. Trost and M.J. Bogdanowicz, J. Am. Chem. Soc. <u>95</u>, 5298 (1973) and <u>95</u>, 5307, 5311 (1973)
- 5) In a typical experiment 1.2 equiv. of triphenyl arsine was added to a solution of cinnamyl bromide in acetonitrile. After stirring at room temperature for 72 h., the solvent was removed under vacuum. The residue was dissolved in methylene chloride and the salt precipitated by adding ether. Yield : 85%
- 6) J.B. Ousset, C. Mioskowski and G. Solladié, Synth. Commun. in the press.
- 7) The cis/trans ratio was generally between 60/40 to 40/60.

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