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EFFECT OF SOLVENT AND BASE ON THE REACTIVITY OF SEMI-STABILIZED ARSONIUM YLIDES

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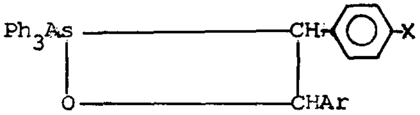
Continuing our studies[1,2] on the factors which influence the course of olefination or epoxidation of cyclic transitional intermediate (I) presently we wish to report the formation of different products in the reaction of benzylidene triphenylarsenane (2a) and p-chlorobenzylidene-triphenylarsenane (2b) with carbonyl compounds, influenced by the nature of solvent and base used in addition to the factors reported earlier[3].



(I)

The ylides (2a, 2b) were generated by dehydrohalogenation of benzyltriphenylarsonium bromide (1a) and p-chlorobenzylitriphenylarsonium bromide (1b) using NaH in benzene or C_2H_5ONa in ethanol.

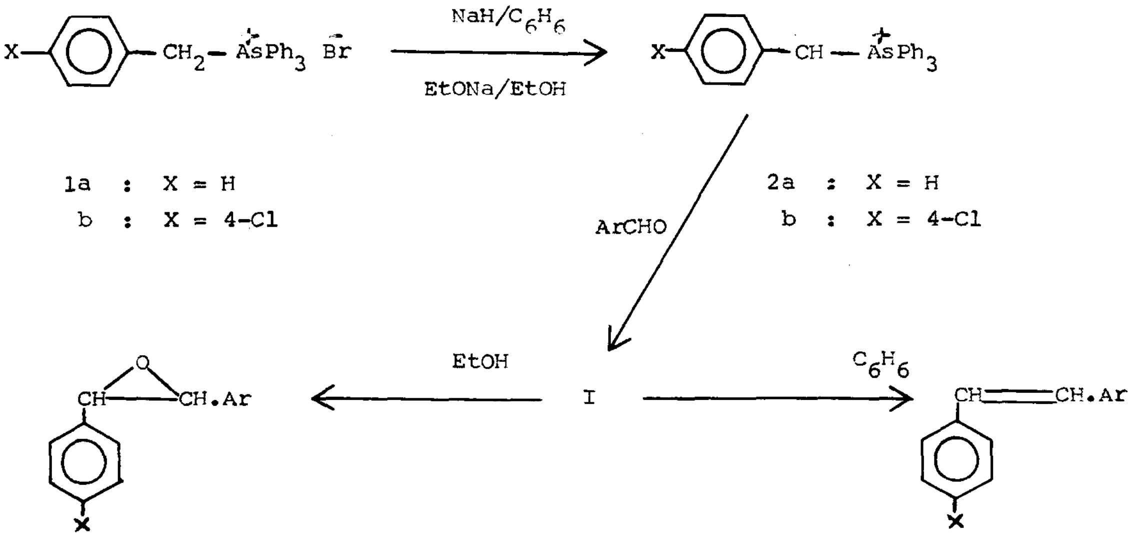
The reaction of ylides (2a, 2b), generated from C_2H_5ONa in ethanol, with a series of substituted benzaldehydes gave epoxides** (3a-3c) exclusively (Scheme I) regardless to the nature of substituents present on aromatic aldehyde, which was in accordance with report of Trippett etal[3].

However, ylides (2a-2b) followed different path, olefination, when sodiumhydride-benzene was used as base-solvent pair. Thus, the ylides (2a, 2b) reacted with series of aldehyde gave olefins+ (4a-4e) (Scheme I), in contrast to the report of Trippett etal.[3] These observation clearly shows that base and solvent, in addition to the nature of substituent present on ylidic carbenion, plays an important role in dictating the exact path of the reaction.

** The reactions were carried out at room temperature for 24 hrs. Solvent was then evaporated and extracted with chloroform. The extract was washed with water; dried, and evaporated and then residue was chromatographed on basic alumina. Elution with P.F.(40-60°)-benzene gave epoxides which were identified by comparison with authentic samples.

+ The reactions were run at room temperature for 3 days. Following the similar procedure used for epoxides, elution with P.E.(40-60°)-benzene (1:2) gave olefins (4a-4e) which were identified by comparison with literature melting point.

Scheme I



1a : X = H
b : X = 4-Cl

2a : X = H
b : X = 4-Cl

3a : X = H; Ar = 4-$NO_2C_6H_4$
b : X = H; Ar = 4-$OCH_3C_6H_4$
c : X = 4-Cl; Ar = 4-$NO_2C_6H_4$

4a : X = H; Ar = 4-$N(CH_3)_2C_6H_4$
b : X = H; Ar = 4-$CH_3C_6H_4$
c : X = 4-Cl; Ar = 4-$NO_2C_6H_4$
d : X = 4-Cl; Ar = 4-ClC_6H_4
e : X = 4-Cl; Ar = 4-$OCH_3C_6H_4$

The structure of the epoxides (3a-3c) and olefins (4a-4e) were confirmed by IR and NMR spectral studies.

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