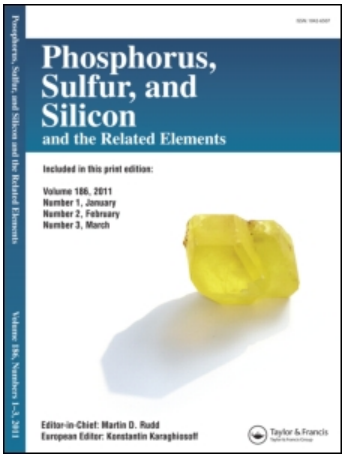

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Petrova, Jordanka , Momchilova, Snejana and Kirilov, Marko(1990) 'Olefin Synthesis via, the Li-Derivative of N,N,N',N'-Tetramethyldimides of Arylmethanephosphonic Acids', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 173 — 178
To link to this Article: DOI: 10.1080/10426509008038934
URL: http://dx.doi.org/10.1080/10426509008038934

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 173-178
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OLEFIN SYNTHESIS VIA THE Li-DERIVATIVE OF N,N,N',N'-TETRAMETHYLDIAMIDES OF ARYLMETHANEPHOSPHONIC ACIDS

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Abstract The high erythro-stereoselective reaction of Li-tetramethyldiamides of arylmethanephosphonic acids with carbonyl compounds is used for synthesis of (Z)-alkenes by thermolysis of the erythro-adducts as well as in acidic media.

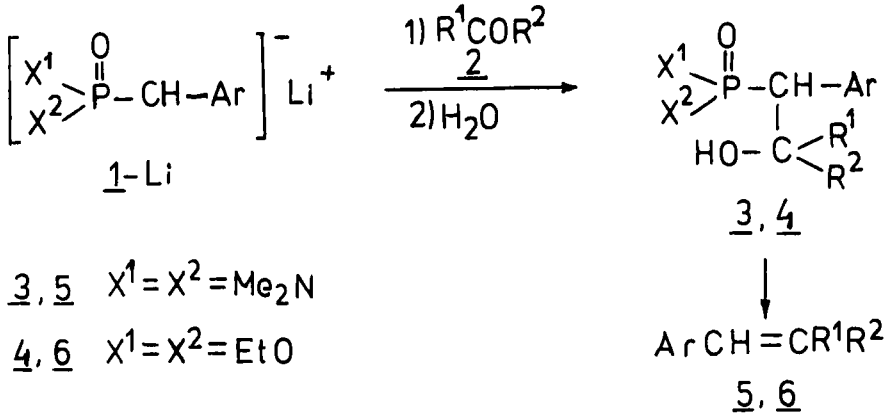
INTRODUCTION

It is known from the literature[1] that (Z)-alkenes are rather difficulty accessible by the Horner-Emmons reaction, because it proceeds in a highly (E)-stereoselective manner. (Z)-Alkenes can be obtained by resolving diastereomeric mixtures of hydroxyphosphonamide[2] or phosphinoxide[3] adducts, followed by stereospecific olefination of the erythro-adducts or their alkaline salts. This approach hovever is not suitable in most of the cases, because the stereoselectivity is lost when Ar or other conjugated groups are in α-position to the PO group.

RESULTS AND DISCUSSION

We found that a large number of (Z)-stilbenes as well as β-mono and disbstituted styrenes can be easily obtained in high diastereomeric purity by achieving a high erythro diastereoselectivity (95-99%) of the reaction between the Li-reagent of tetramethyldiamides of arylmethanephosphonic acids and carbonyl compounds, following by stereospe-

cific olefination of the erythro-adducts. This way, the corresponding (Z)-alkenes were obtained in good yield and high (Z)-diastereomeric purity (95-99%)[4-6].



3 R^2=H erythro/threo = 95/5

5 R^2=H Z/E = 95/5

SCHEME 1.

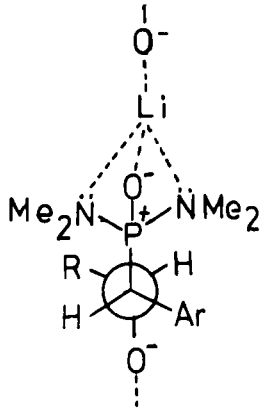
We studied also the interaction of the Li-reagent with ketones. The yields of the olefins, obtained by Horner-Emmons reaction are very low in the cases of enolyzable ketones[6]. We studied the reaction with some alkanones, cycloalkanones, arylalkyl and diaryl ketones[7]. Further, by thermal olefination of the adducts the corresponding alkenes were obtained (60-80% yields). Thus the described reaction represents a convenient synthetic pathway for alkenes even from enolyzable ketones.

Recently we succeded to stop the reaction of Li-derivative of diethyl ester of phenylmethanephosphonic acid (Scheme 1, X^1=X^2=EtO) with carbonyl compounds at the aldol stage. The stereoselectivity is low, with some ketones threo isomers predominate. Our results show that when X^1=X^2=Me_2N the erythro-adducts 3 are thermodinamically controlled products in contrast to meny other cases of the Wittig-Horner reaction. This unexpected fact was confirmed by the complete conversion of the threo-isomer into erythro

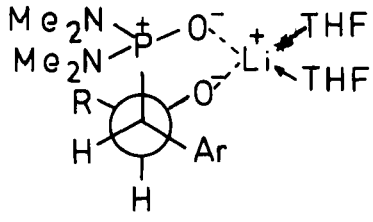
in conditions of thermodinamic control, i.e.

threo-3 $\xrightarrow{BuLi}$ threo-3-Li $\longrightarrow$ 1-Li + 2 $\longrightarrow$ erythro 3

This result was explained with the formation of a very stable complex of 4-coordinated Li^+ in the metal derivative of erythro isomers du to a chain-polymer association (Fig. 1).



erythro - 3-Li



threo - 3-Li

FIGURE 1. Possible conformations of 3-Li

The relative configurations and favoured conformations of the isolated adducts were determined by NMR and IR spectral data. On the bases of IR-spectra in deluted (10^{-3}M) CCl_4 solution and the vicinal H-H coupling constant as well as the H-P coupling constants it is concluded that the erythro-isomers exist preferably in conformation E_1, i.e. $E_1 \gg E_2$ and E_3. (Figure 2). For threo-isomers the preferable conformation depends on the substituents in the benzene ring of the starting aldehyde. For unsubstituted or p-substituted threo-isomers $T_1 > T_2 \gg T_3$. In the cases with ortho substituents as well as in the case of the adduct with acetophenon the part of the conformation T_2 increases. On the basis of the J constant value for the methyl group ($^3J_{CH}$=6.4 Hz) and taking into account the

Carplus dependence of J on the dihedral angle, it canbe assumed that $T_2 \approx T_1 \gg T_3$.[8]

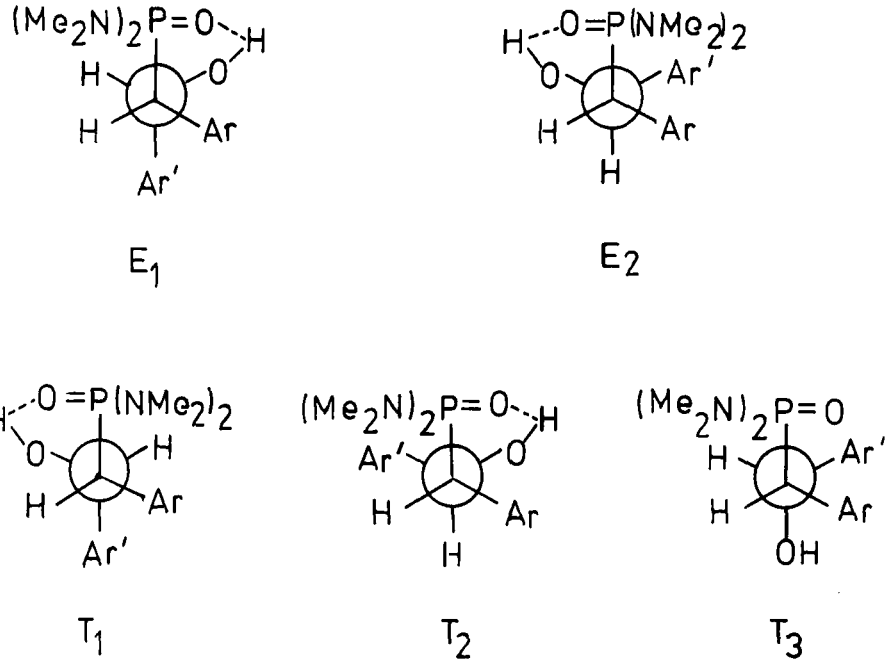
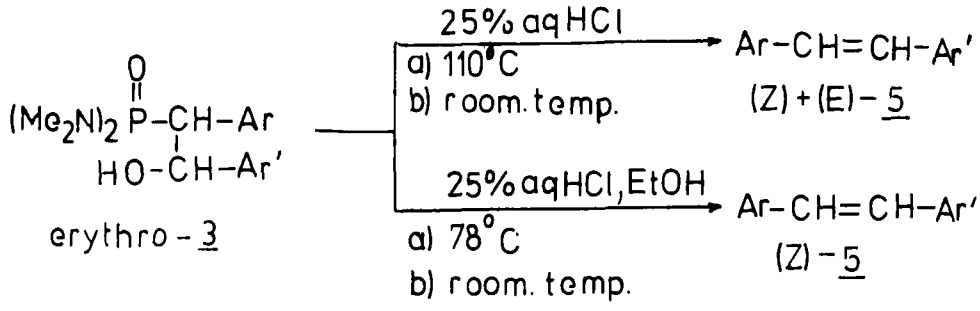


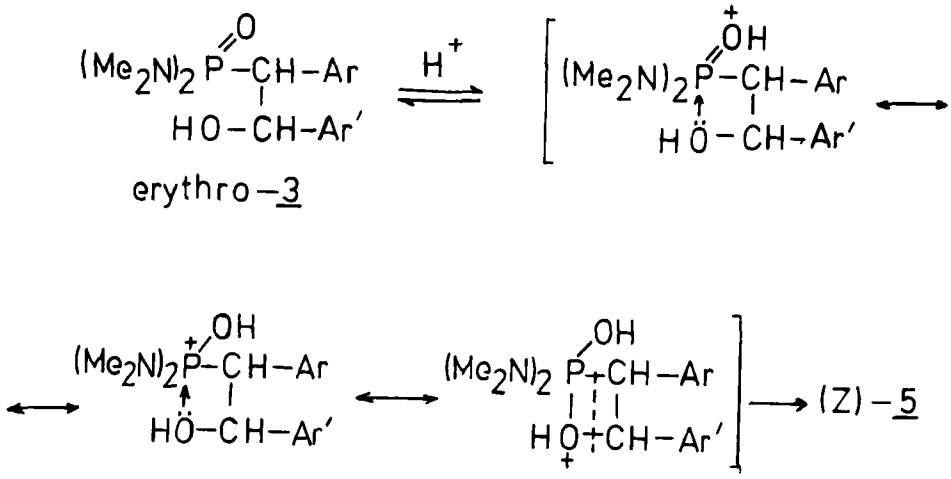
FIGURE 2. Possible conformations of erythro and threo-3

In all experiments for synthese of Z-alkenes we applied the Corey elimination procedure as a second stage of the carbonylolefination. The high temperature, required in this stage, is a shortcoming in thermal olefination. For that reason we studied the olefin formation in acid medium[9]. We found that in aqueous hydrochloric acid in all cases the reaction proceeds not stereospecifically. In ethanol in the presence of hydrochloric acid at room temperature or at reflux, however, practically pure cis-alkenes were obtained, that is Z-stereospecific olefin formation takes place (Scheme 2). The Z-stereospecific cleavage probably proceeds as syn elimination via cyclic intermediate. In this case the acid probably increases the



SCHEME 2.

electrophility of the phosphorus atom (Scheme 3.). This mechanism for the olefination in ethanol is in accordance with the data of our preliminary experiments on the kinetics of the reaction. The high negative value of the entropy of activation $\Delta S^{*} = -18\ kJK^{-1}mol^{-1}$ proves a mechanism with formation of cyclic intermediate.



SCHEME 3.

It was experimentally proved that the direct isomerisation Z-stilbene $\rightleftharpoons$ E-stilbene does not take place in the reaction conditions.

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