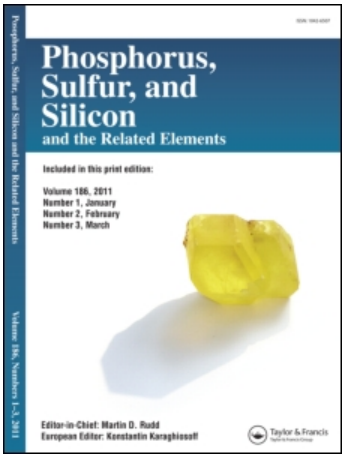

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New Chemistry of Enol Phosphates

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NEW CHEMISTRY OF ENOL PHOSPHATES

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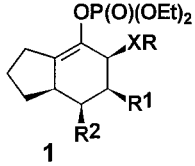
Applications of enol phosphates in the synthesis of novel bicyclic 1,3-dienes, bi- and polycyclic aromatic derivatives, and α-hydroxy ketones are described.

Keywords: Cyclic 1,3-dienes; enol phosphates; α-hydroxy ketones; polycyclic aromatic compounds

INTRODUCTION

The biological activities of enol phosphates are of considerable interest, and as a consequence many methods have been devised for their preparation.[1] However, the utility of enol phosphates in organic synthesis is severely limited.

We have previously described[2] regio- and endo-stereospecific synthesis of novel bi- and polycyclic enol phosphates **1** via the Diels-Alder reactions of our 1,3-dienes[3] with a number of dienophiles.



1

X = S, Se

1a: R^1 = CN, R^2 = H; 1b: R^1 = C(O)Me, R^2 = H; 1c: R^1 = CO_2Et, R^2 = H

1d: R^1 = CHO, R^2 = H; 1e: R^1 = CN, R^2 = CN; 1g: R^1, R^2 = CO_2Me

1h: R^1 - R^2 = -C(O)NPhC(O)-; 1i: R^1 - R^2 = $-C(O)CH_2CH_2C_2CH_2-$

Now we report on the synthetic applications of enol phosphates in the preparation of important organic compounds, such as bicyclic 1,3-dienes, bi- and polycyclic aromatic compounds, and acyclic and cyclic α-hydroxy ketones.[4,5]

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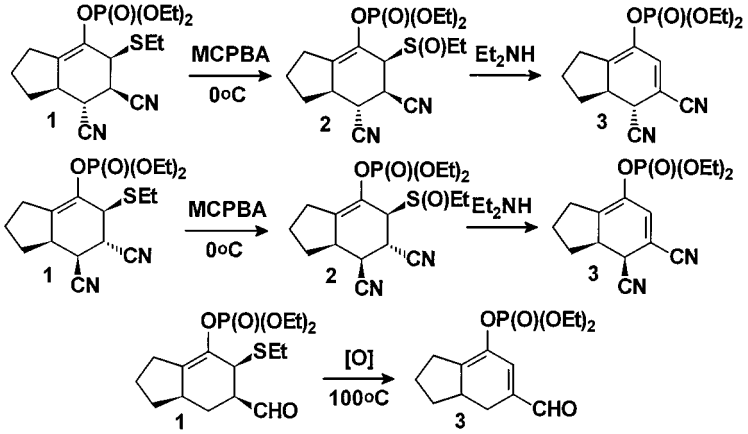
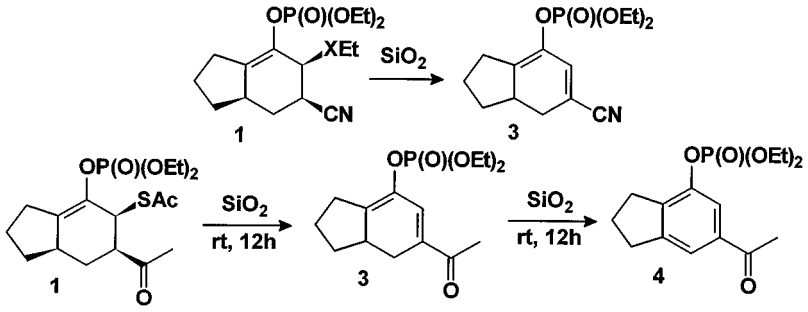
RESULTS AND DISCUSSION

We have found that elimination reactions of enol phosphates to form bicyclic conjugated dienes can be performed in the following way: oxidation of the sulfide moiety of the enol phosphates (using MCPBA to give the sulfoxide, which has better properties as a leaving group) and then treatment with diethylamine afforded 1,3-dienes **3** in good yield. When oxidation is performed at 100°C, elimination proceeds without the help of an amine (Scheme 1).



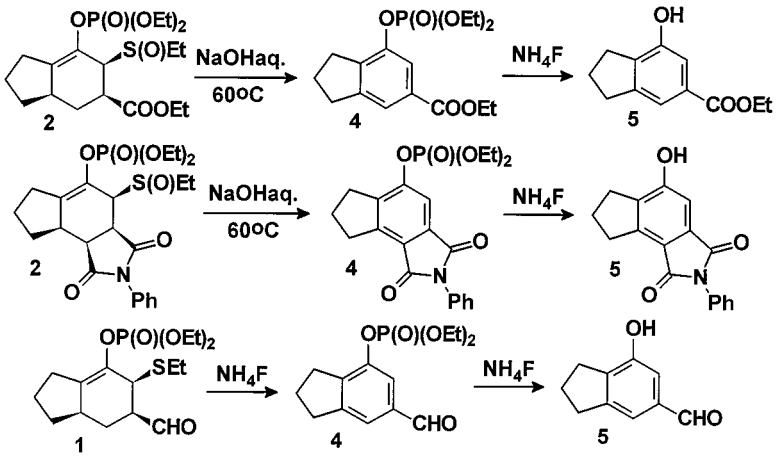
SCHEME 1

An efficient way to catalyze elimination of the sulfur (selenium) substituent is to deposit the enol phosphates in benzene/AcOEt 2:1 solution on silica gel at room temperature overnight, but after a further 12 h the 1,3-diene **3** aromatises to arene derivative **4** (Scheme 2).



SCHEME 2

We have also synthesized other types of aromatic compounds **4** by warming enol phosphates **2** containing a sulfoxide function at 60°C for 1 h in an aq. solution of sodium hydroxide or by the action of ammonium fluoride on **1**. It is well known that the fluoride anion is an excellent nucleophile towards phosphorus atoms. Indeed, **4** was easily converted into hydroxy arene derivatives in good yield by treatment with fluoride anion (Scheme 3).

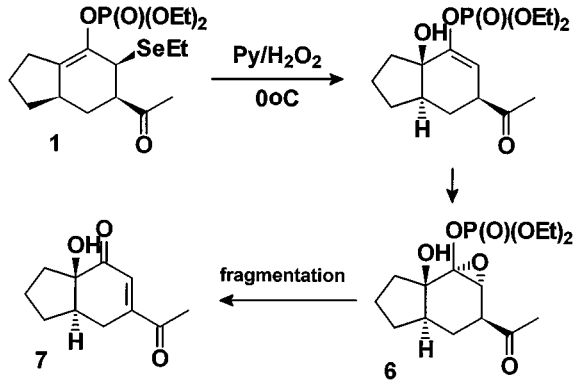


SCHEME 3

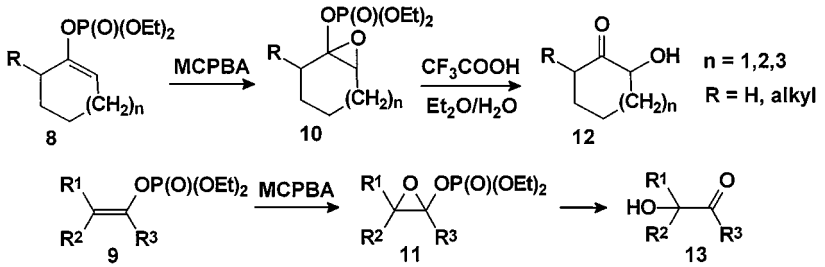
Recently, we have elaborated the stereospecific synthesis of bi- and polycyclic allylic alcohols containing an enol phosphate function via [2,3]-sigmatropic rearrangement of enol phosphates **2**.[2] We have also found a new route to α-hydroxy ketones. Oxidation of enol phosphate **1** containing a selenide substituent with excess hydrogen peroxide in the presence of pyridine provides the epoxy enol phosphate **6** via an intermediate allylic alcohol. **6** collapses under the reaction conditions to the bicyclic functionalized α-hydroxy ketone **7**[2] (Scheme 4).

This result prompted us to develop the methodology based on epoxy phosphate intermediates to an alternative, general synthesis of α-hydroxy ketones. Oxidation of cyclic **8** and acyclic **9** enol phosphates by the action of MCPBA provided quite stable epoxy enol phosphates **10** and **11**, respectively, in good yield. Opening of the epoxide ring with elimination of diethyl phosphoric acid was performed with 25% trifluoroacetic acid in ether/water 1:1 solution giving α-hydroxy ketones **12** and **13** in good yield (Scheme 5).

The structures of all compounds described were confirmed by NMR and MS data.



SCHEME 4



SCHEME 5

In summary, we have demonstrated the synthetic utility of enol phosphates. The attractiveness of these compounds lies in the ease with which they can be transformed into novel bicyclic 1,3-dienes, bi- and polycyclic aromatic compounds, and α-hydroxy ketones.

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