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Preparation of Functionalized Cyclobutenones and Phenolic Compounds from α-Diazo β-ketophosphonates

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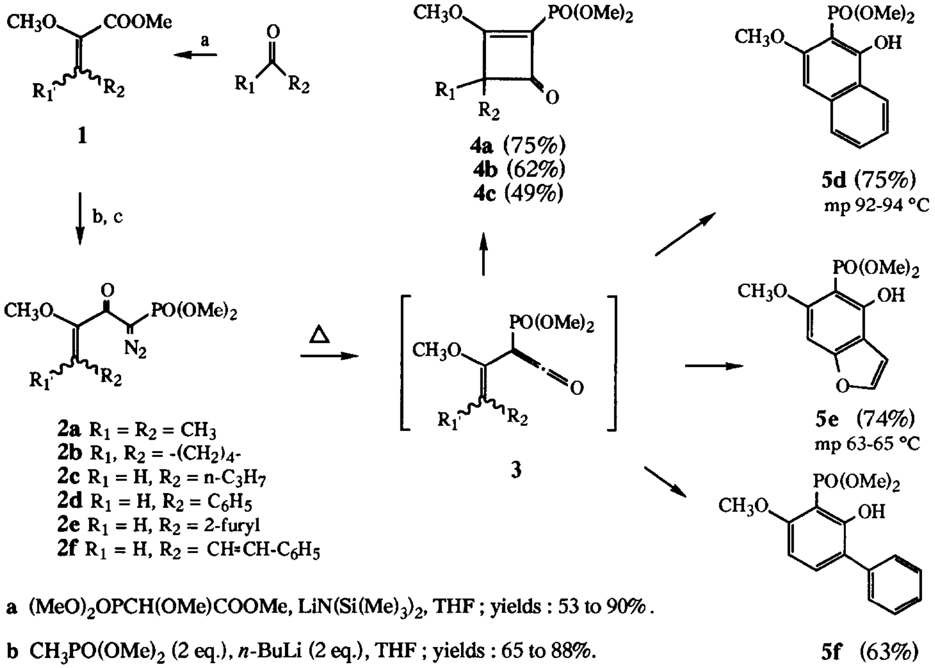
Abstract : *When heated in refluxing benzene or toluene, α-diazo β-ketophosphonates 2, prepared in three steps from aldehydes or ketones, gave rise to functionalized cyclobutenones 4 or phenolic compounds 5. These products are formed by electrocyclisation respectively of a vinyl or dienylketene, resulting from a Wolff rearrangement.*

The methyl 2-methoxy-2-alkenoates **1** are readily obtained from aldehydes or ketones by a Wadsworth Emmons reaction using methyl 2-methoxy-2-dimethylphosphono acetate.[1] Pursuing our investigation on the usefulness of these compounds[2], as well as their 2-trialkylsilyloxy analogs[3], we describe in this note some synthetic potentialities of α-diazo β-ketophosphonates **2** easily obtainable in two steps from **1**. We expected that a thermally induced Wolff rearrangement[4] of compounds **2** would generate an intermediate ketene susceptible to electrocyclic ring closure giving rise to functionalized carbocycles.

From saturated keto compounds, we first prepared **2a**, **2b** and **2c**. When a benzene solution of these compounds was heated to reflux (**2a**, 22 h; **2b** or **2c**, 48 h) the cyclobutenones **4** were obtained, through the intermediate vinylketene **3**[5], in moderate to good yields.[6]

Since dienylketenes are known to undergo 6π electrocyclisation followed by tautomerization to yield phenols derivatives[7,8], we then prepared diazo ketophosphonates **2d**, **2e** and **2f** bearing an additionnal conjugated carbon-carbon double bond. In a first experiment, the two stereoisomers **2d-E** and **2d-Z** were heated separately in refluxing benzene (30 h) or toluene (3 h). Since they both led to the expected naphtol **5d** in about the same yield, we then treated a mixture of the Z and E isomers of **2e** or **2f** under the above conditions and obtained **5e** and **5f** in good yield. The formation of compounds **5** from either the Z or E isomer of diazo ketophosphonates **2** can be explained as follows. The E isomer can give rise to **5** by electrocyclisation of the corresponding intermediate dienylketene **3E** having the required stereochemistry. The Z isomer would first lead to a vinyl cyclobutenone of type **4** which would reopen in either **3E** or **3Z** and finally lead to compounds **5**.

However, we did not observe (TLC) the formation of the intermediate cyclobutenones **4** during the course of the reaction.



a $(MeO)_2OPCH(OMe)COOMe$, $LiN(Si(Me)_3)_2$, THF ; yields : 53 to 90%.

b $CH_3PO(OMe)_2$ (2 eq.), *n*-BuLi (2 eq.), THF ; yields : 65 to 88%.

c TsN_3, K_2CO_3, CH_3CN ; yields : 52 to 84% .

In conclusion, we describe in this note the preparation in four steps, from aldehydes or ketones, of either functionalized cyclobutenones or phenolic compounds depending on the starting keto compound. We are currently exploring the further synthetic possibilities of this sequence.

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