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# (3,3-DIISOPROPOXYPROPYL)TRIPHENYLARSONIUM YLIDE : A NEW SYNTHETIC EQUIVALENT OF β-FORMYL VINYL ANION

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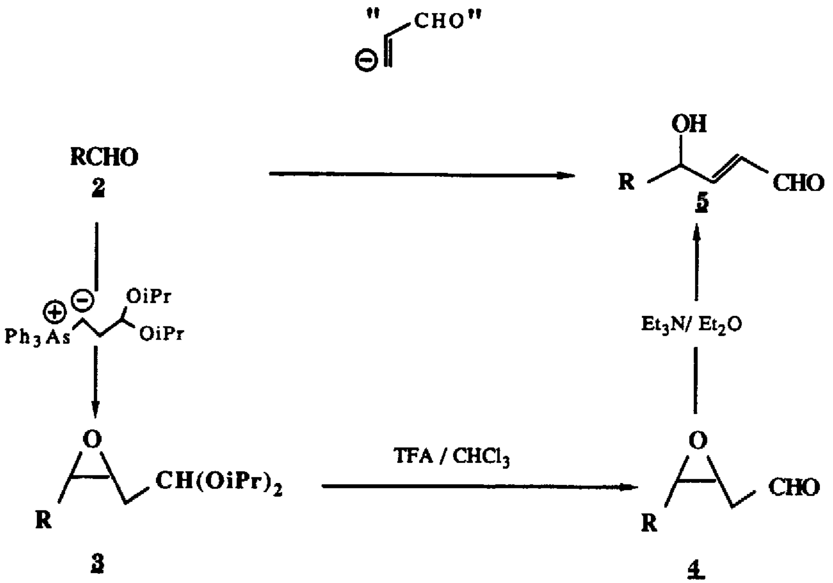
Summary: *The synthesis and the reactivity of (3,3-diisopropoxypropyl) triphenylarsonium ylide are described. This new reagent can be considered as a β-formyl vinyl anion equivalent, as shown by the conversion of aldehydes to 4-hydroxy-2-(E)-enals in very mild conditions.*

Since Corey and coll.[1] described 1,3-bis (methylthio)propene as an effective β-formyl vinyl anion equivalent, much interest has been devoted to the preparation of new reagents bearing $d^3$ inverted polarity[2] and leading to β-substituted enals. These reagents generally involve heterosubstituted allyl[3]-, allenyl[4]- or propargyllithium[5] metallated intermediates, which are not always compatible with sensitive functionalities found in complex organic structures[6]. During the course of our synthetic work, we had to convert aldehyde **2** to the corresponding γ-hydroxy-enal **5** under very mild conditions. Therefore, we developed a new β-formyl vinyl anion equivalent : (3,3-diisopropoxypropyl)-triphenylarsonium ylide **1** ( scheme 1).

**1**

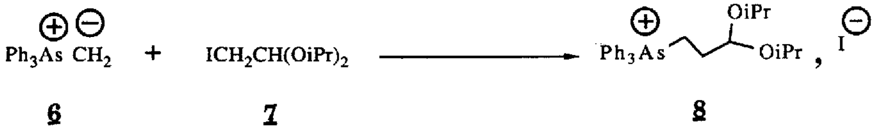
SCHEME 1

Stabilized arsonium ylides provide alkenes while the non-stabilized ones give epoxides[7]. Semi-stabilized ylides generally give rise to mixtures[8], where the ratio of alkenes and epoxides can be monitored by the solvent system used[9]. Efforts have been recently expanded to develop the chemistry of stabilized functionalized arsonium ylides[10] which have been successfully used in the synthesis of natural products[11]. In the case of non-stabilized ylides, only a few reports have appeared in the literature[12]. We report herein our results related to the synthesis and the reactivity of the non-stabilized, functionalized arsonium ylide **1** ( scheme 2 ).



SCHEME 2

By analogy with the synthesis of the corresponding phosphonium salt[13], attempts to obtain the arsonium salt **1** from triphenylarsine, acrolein and hydrogen bromide failed. Condensation of methylene triphenylarsonium ylide **6**[14] with 2-iodo-1,1-diisopropoxy-ethane **7** in THF / HMPA leads to the desired arsonium salt in 80% yield after recrystallization from methylene chloride / ether ( scheme 3 ).



SCHEME 3

Arsonium ylide **1** was generated at -40°C in THF with LDA 0.3M and then condensed with aldehydes **2** (a-e) at -78°C. The β-epoxyacetals **3**, obtained in fair yields after purification on silicagel, were easily deprotected with trifluoroacetic acid in chloroform at room temperature. The β-epoxyaldehydes **4** were then directly isomerized to the corresponding γ-hydroxy-enals **5** with an excess of triethylamine in ether, at room temperature[15]. Final purification was performed by flash chromatography on silicagel. The results are summarized in table 1.

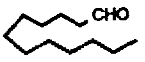
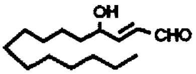
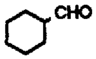
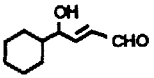
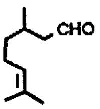
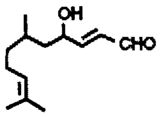
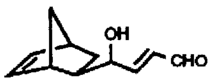
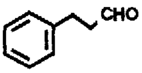
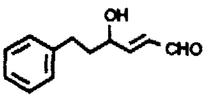
| Entry | Aldehydes **2** | epoxidation **2** → **3** Yield % | γ-Hydroxy-enals **5** | **3** → **5** Yield % |
|---|---|---|---|---|
| a |  | 70 |  | 65 |
| b |  | 62 |  | 82 |
| c |  | 69 |  | 79 |
| d |  | 56 |  | 71 |
| e |  | 68 |  | 86 |

TABLE 1

In conclusion, aldehydes can be converted to γ-hydroxy-enals in a three step sequence under very mild conditions. In this formal vinylogous formyl anion transfer, one may view arsonium ylide **1** as a new "Umpolung" reagent. This route has been successfully applied to the total synthesis of hepoxilin $A_3$, which will be described in due course.

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