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# Allylic Phosphates as Allyl Anion Synthons. Lithium-induced Allylation of Carbonyl Compounds

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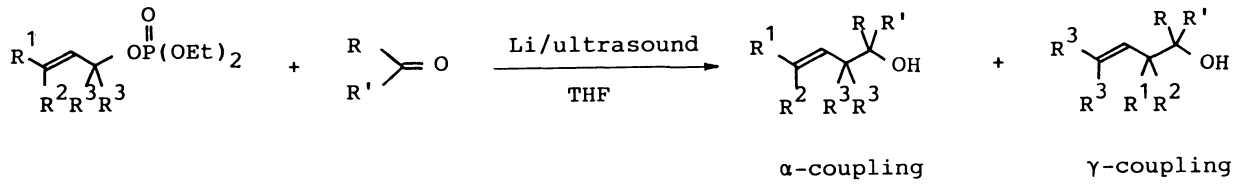
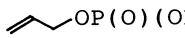
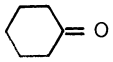
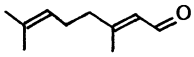
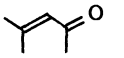
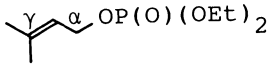
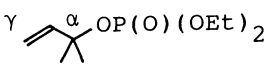
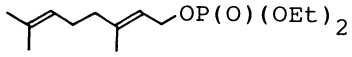
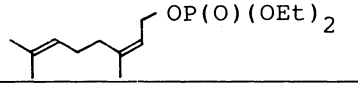
Ultrasonication of allylic phosphates and carbonyl compounds with a lithium powder gave high yields of the corresponding homoallylic alcohols.

Allylic phosphates, easily accessible by the phosphorylation of allylic alcohols,[1] are useful reagents in synthetic chemistry. They possess several advantages over allylic halides in regard to reactivity, selectivity, and ease of manipulation.[2] They react usually with nucleophiles, working as allyl cation synthons. On the other hand, their use as allyl anion equivalents has been strictly limited. Very recently, allylation of carbonyl compounds by allylic phosphates was achieved using chromium(II) chloride,[3] samarium(II) iodide,[2] and metallic antimony.[4] Here, we describe a convenient allylation of carbonyl compounds which involves the ultrasound irradiation[5] of a mixture of allylic phosphates and carbonyl compounds with a lithium powder.




Typical experimental procedure is as follows. A mixture of allyl diethyl phosphate (190 μl, 1 mmol), benzaldehyde (50 μl, 0.5 mmol), and a lithium powder (31 mg, 4.4 mmol) in anhydrous tetrahydrofuran was ultrasonicated under argon. Exothermic reaction occurred immediately and the reaction went to completion within 3 min. The mixture was poured into saturated aqueous ammonium chloride and the product was extracted with ether. Purification by column chromatography on silica gel gave 1-phenyl-3-buten-1-ol (63 mg, 85%). The results for various phosphates and carbonyl compounds are summarized in Table 1, which illustrates the following characteristics: a) Various types of carbonyl compounds (aldehyde, ketone, ester, and acid chloride) reacted readily to give high yields of the corresponding homoallylic alcohols. b) α,β-Unsaturated carbonyl compounds (entries 5 and 6) gave only 1,2-addition products. c) Regioselectivity (α vs. γ) of allylic systems was poor and the mixtures of α- and γ-coupling products

Table 1. Lithium-mediated Allylation of Carbonyl Compounds by Allylic Phosphates[a)]

| Entry | Phosphate | Carbonyl compound | Yield/% | Remark |
|---|---|---|---|---|
| 1 |  | PhCHO | 85 | |
| 2 | | $C_7H_{15}CHO$ | 83 | |
| 3 | |  | 83 | |
| 4 | | $PhCOCH_3$ | 99 | |
| 5 | |  | 100 | 1,2-Addition only |
| 6 | |  | 90 | 1,2-Addition only |
| 7[b)] | | $C_7H_{15}CO_2CH_3$ | 90 | Product: $C_7H_{15}C(OH)(CH_2CH{=}CH_2)_2$ |
| 8[b)] | | $C_7H_{15}COCl$ | 79 | Product: $C_7H_{15}C(OH)(CH_2CH{=}CH_2)_2$ |
| 9 |  | PhCHO | 100 | α : γ = 31 : 69 |
| 10[c)] | | PhCHO | 95 | α : γ = 6 : 94 |
| 11 | | $C_6H_{13}COCH_3$ | 82 | α : γ = 5 : 95 |
| 12 |  | PhCHO | 93 | α : γ = 71 : 29 |
| 13[c)] | | PhCHO | 89 | α : γ = 87 : 13 |
| 14[d)] |  | PhCHO | 84 | α : γ = 78 : 22 |
| 15[d)] |  | PhCHO | 79 | α : γ = 80 : 20 |

a) All the reactions were carried out under the ratio of phosphate : carbonyl compound 2 : 1, unless otherwise noted. b) Phosphate : carbonyl compound 3 : 1. c) In the presence of 10 mol% of CuI. d) Double bond geometry was completely retained.

were obtained. The selectivity largely depended on the substitution pattern of allylic systems (entries 9, 12, 14, and 15). A catalytic amount of copper(I) iodide increased the regioselectivity (entries 10 and 13). Entries 9 and 12 suggest the common intermediate lithium species, 3,3-dimethylallyllithium. d) Double bond geometry of allylic double bond was completely retained.

The present method is superior to the existing ones[2-4)] in regard to high yields, short reaction time, and operational simplicity, and therefore, provides a convenient method for the in situ generation of allylic lithium reagents under mild conditions. Synthetic applications of this Barbier-type coupling are now in progress.

References

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2) S. Araki, H. Hatano, H. Ito, and Y. Butsugan, J. Organomet. Chem., 333, 329 (1987); and references cited therein.
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4) Y. Butsugan, H. Ito, and S. Araki, Tetrahedron Lett., 28, 3707 (1987).
5) Ultrasound in organic synthesis; see: P. Boudjouk, J. Chem. Educ., 63, 427 (1986)

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