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ENOLATE ALKYLATIONS WITH DIETHYLBUTADIENE PHOSPHONATE-II

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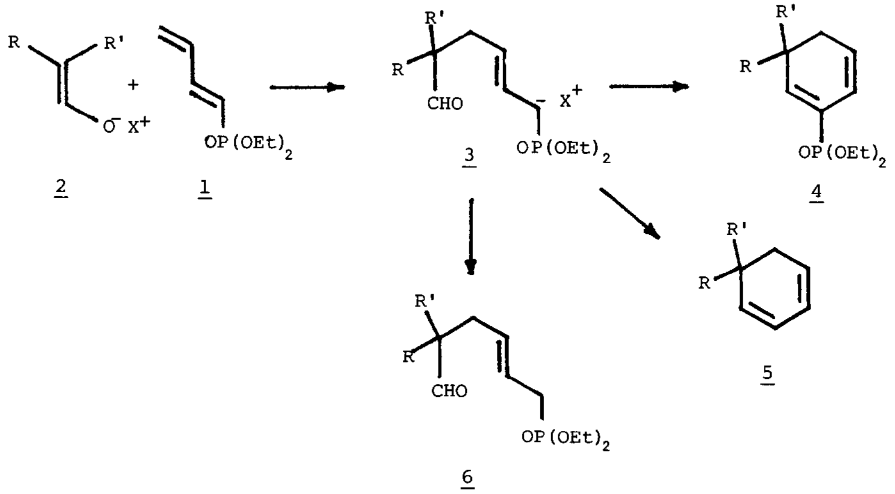
An effect by the cation has been observed in the reactions of aldehyde enolates with 1-diethylphosphinyl-1,3-butadiene.

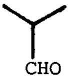
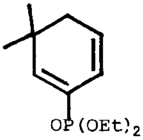
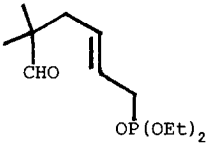
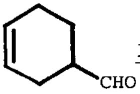
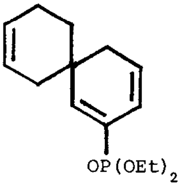
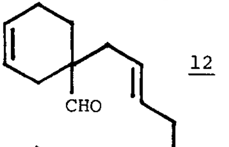
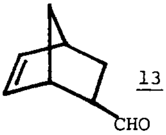
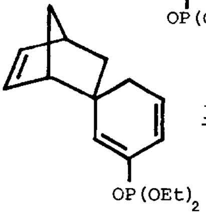
The unusual reactivity of the diethylbutadiene phosphonate 1 towards ketone enolates[2] prompted us to examine the reaction of 1 with certain aldehyde enolates. Aldehydes with only one alpha proton were chosen for this investigation. Such a reaction, in principle, should lead to one or more of the following products.



Generation of the lithium enolate by Method A (treatment with equimolar LDA) followed by the addition of the dienephosphonate 1 yielded the product 4 whereas production of the ammonium enolate via the silyl enol ether (Method B)[3] and benzyltrimethylammonium fluoride afforded the product 6. In one example the potassium enolate of isobutyraldehyde 7 also yielded the uncyclized product 9. In the few examples studied, compound 5 resulting from Wadsworth-Emmons[4] elimination was not obtained. The results are summarized in the Table.

The difference in reactivity of the lithium and the ammonium enolates could be due to the effect of the respective cations. The compound 8 has been previously prepared by the cycloaddition of 1 with the pyrrolidine enamine of isobutyraldehyde followed by the elimination of pyrrolidine.[7]

The formation of the cross-conjugated dienephosphonates such as 4 might have arisen from the initial Michael addition of the enolates to 1 followed by an aldol condensation and dehydration.[8,9] In essence, three reactions are carried out in one reaction vessel. The synthetic utility of 1 as a spiro-annelation reagent is also demonstrated by the formation of 11 and 14.

Substrate	Procedure	Product[5]	Isolated Yield[6] %
 7	Method A	 8	33
7	Method B	 9	49
 10	Method A	 11	26
10	Method B	 12	45
 13	Method A	 14	22

REFERENCES

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2. See previous communication, this journal.
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4. W. S. Wadsworth and W. D. Emmons, J. Amer. Chem. Soc., 83, 1733 (1961).
5. All the products were characterized by NMR, IR, MS, UV and elemental analysis.
6. Yields were not optimized.
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