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A STEREOSPECIFIC PHOSPHONIUM YLIDE-SALT COUPLING REACTION

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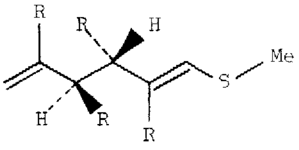
Abstract The stereospecific formation of a phosphonium ylide-salt *via* the stereospecific coupling of an allylic phosphonium ylide with the corresponding phosphonium salt is described

In recent contributions[1-7] from this laboratory a stereospecific sulphonium ylide-salt coupling reaction, leading to the formation of the vinyl sulphide (1) *via* Michael addition of the sulphonium ylide (2) to the sulphonium bromide (3), followed by demethylation of the resulting salt (4) by bromide ion, was communicated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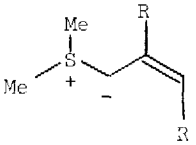
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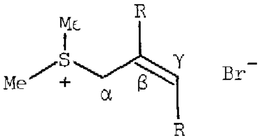
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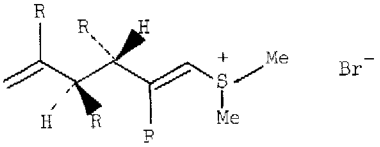
(4)

R = CO_2Me

As an extention of these investigations, it was found that a related coupling reaction took place when a vigorously stirred solution of the phosphonium salt (6) in dichloromethane was treated with one mole equivalent of aqueous sodium hydroxide, to produce the dimeric phosphonium ylide-salt (8)[**] as bright yellow crystals in 50% yield Under these reaction conditions the phosphonium ylide (5) was formed as a by-product in only 20% yield

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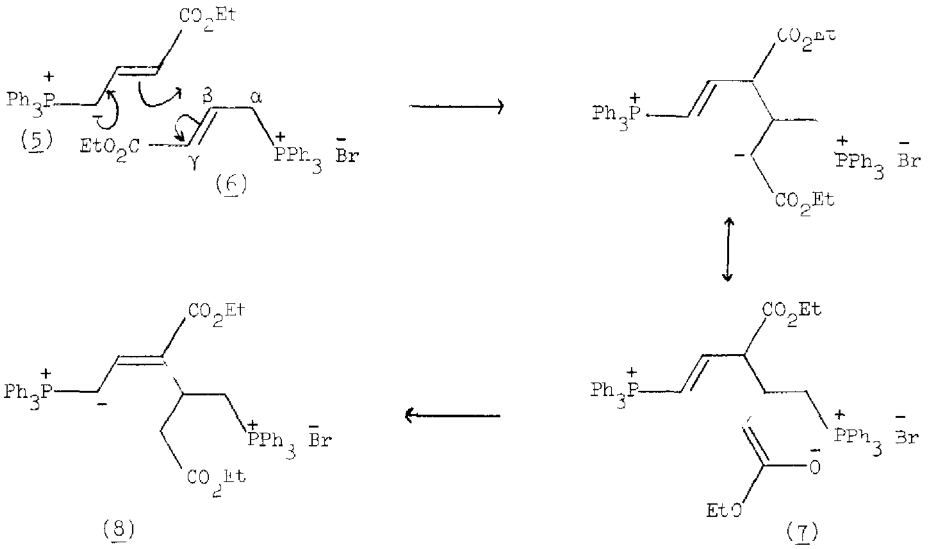
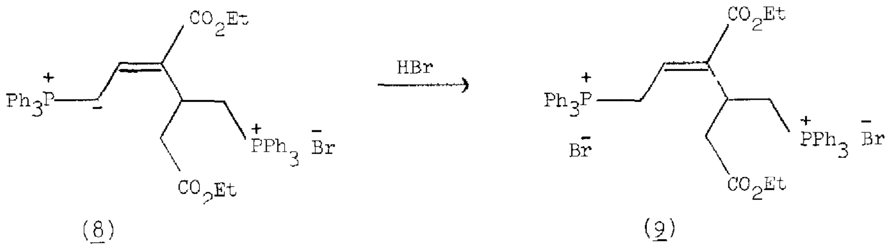
[**] All new compounds exhibited satisfactory analytical data Proposed structures were rigorously substantiated by extensive ^{1}H and ^{13}C nmr studies and off-resonance decoupling experiments

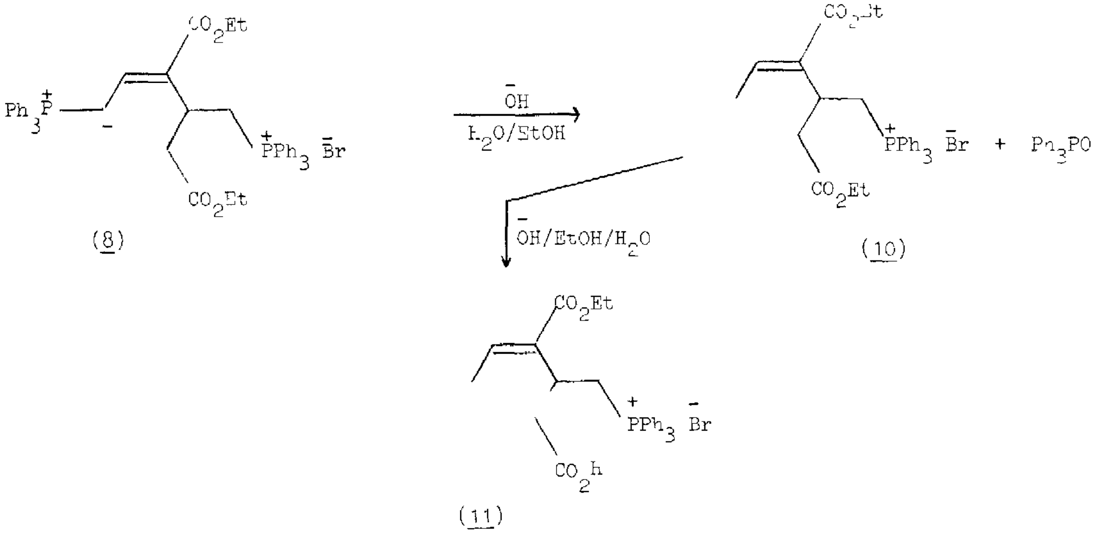


The formation of the ylide-salt (8) under these circumstances can be rationalized as being the result of a Michael addition of the phosphonium ylide (5) to the phosphonium salt (6), followed by *trans*-ylidation of the intermediate product (7). In comparison with the above-mentioned sulphonium ylide-salt coupling reaction where the ylide (2) attacked the salt (3) solely at the γ-carbon atom, it is clear that the absence of a second alkoxycarbonyl substituent at the β-carbon atom of the phosphonium salt (6) inhibited nucleophilic attack by the phosphonium ylide (5) at the γ-carbon atom of the salt (6).

The ylide-salt character of the coupling product (8) was verified by the formation of the colourless diphosphonium salt (9) upon treatment with aqueous hydrobromic acid, and the precipitation of silver bromide when silver nitrate was added to an aqueous solution of (8).

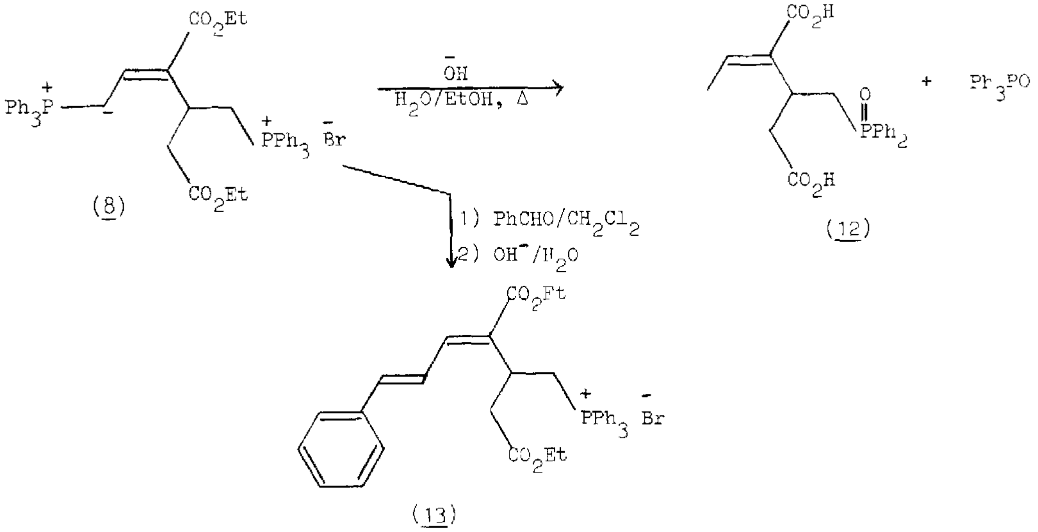


Selective alkaline hydrolysis of the coupling product (8) with one mole equivalent of sodiumhydroxide in 80% ethanol[8] produced one mole of triphenylphosphine oxide and a mixture of the (E)-diester (10) and the (E)-monoester (11).[9] The preferential saponification of the "aliphatic" ethoxycarbonyl group in the presence of an "olefinic" ester substituent is in accord with previous findings.[12,13]



Alkaline hydrolysis of the ylide-salt (8) under more drastic reaction conditions (5 mole equiv of alcoholic NaOH, reflux 15 h) produced as expected, one mole equivalent of triphenylphosphine oxide and the (E)-diphenylphosphine oxide (12) as the sole cleavage products [10,11]

Final proof of the ylide structure of the coupling product (8) was provided by its condensation with benzaldehyde in a Wittig reaction to produce the (E,E)-phosphonium bromide (13) as the only product However, no condensation took place at the phosphonium centre, even when (8) was treated with aqueous base in the presence of an excess of benzaldehyde in two-phase reaction [14]



The coupling product (8) was also produced in 60 and 69% yield, respectively, by reaction of a 1:1 mixture of the phosphonium bromide (6) and the ylide (5) in dichloromethane, and upon treatment of a solution of a salt (6) in dichloromethane with 0,5 moles of aqueous sodium hydroxide. These results provide decisive proof in favour of the phosphonium ylide-salt coupling mechanism for the formation of the dimeric product (8).

The reaction conditions for the formation of the coupling product (8) can very usefully be adapted to produce the phosphonium ylide (5) instead of (8). Slow, synchronised mixing of one mole each of aqueous sodium hydroxide and a solution of the phosphonium bromide (6) in dichloromethane, produced the pure ylide (5) in *ca* 80% yield without concomitant formation of the ylide salt (8).

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