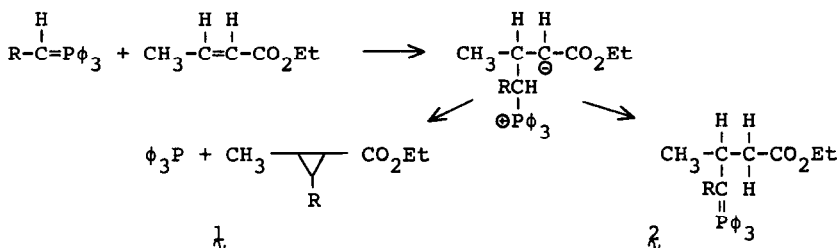


CONJUGATIVE ADDITIONS OF ALLYL YLIDS TO DIENOIC ESTERS:
A NEW SYNTHESIS OF BICYCLO[4.1.0]HEPTENES.¹

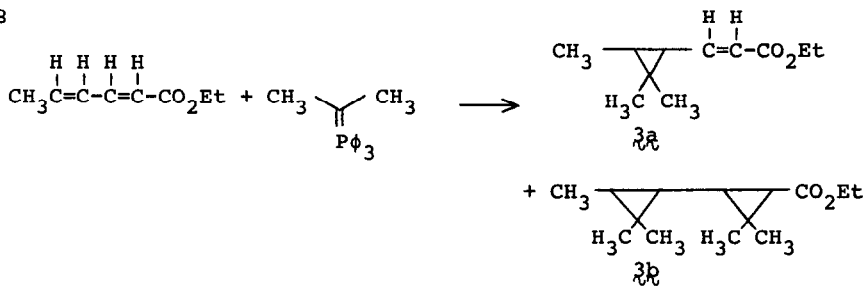
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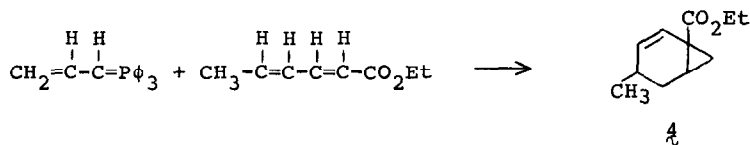
In our studies related to the development of new syntheses of carbocyclic ring systems, we have investigated the reaction of alkylidenetriphenylphosphoranes with conjugated dienoic esters. It has previously been shown that such phosphoranes add in a conjugate fashion to compounds containing an activated double bond.^{3,4,5} In particular, reaction of phosphoranes with α,β -unsaturated esters gives either a cyclopropane derivative λ if R = alkyl or a new ylid λ' if R = resonance stabilized group.^{6,7}



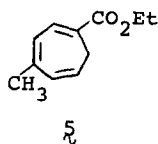
We have found that isopropylidenetriphenylphosphorane does in fact add to ethyl sorbate to form a mixture of the expected cyclopropane derivatives $\lambda'a$ and $\lambda'b$ (1:1).⁸



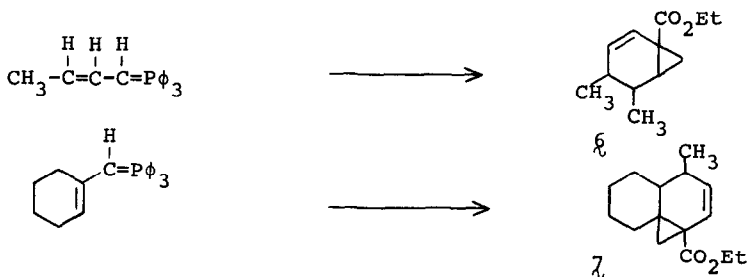
More remarkably, however, we have found that allylidetriphenylphosphorane, which is known to add first from the γ -position of the ylid to unsaturated carbonyl compounds,^{4,5,9} gave the norcar-2-ene **4** on treatment with ethyl sorbate in THF at room temperature; ir(CCl₄) 1725 cm⁻¹; nmr(CCl₄) δ 6.45-5.98 (m, 1), 5.46-4.97 (m, 1), 4.10 (q, 2), 2.40-1.68 (m, 3), 1.68-0.90 (contains 9 H, with t at 1.28 and d at 1.01); mass spectrum (70 eV) m/e 180,165. Evidence for this



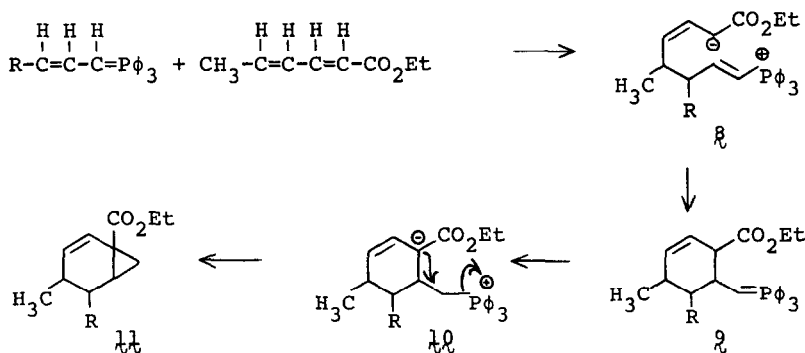
structure was obtained by bromination of **4** at -20^o¹⁰ in CHCl₃ followed by dehydrobromination with DBN in refluxing benzene to give the cycloheptatriene **5**.¹¹



Reaction of butenyldetriphenylphosphorane and (1-cyclohexen-1-ylmethylene)triphenylphosphorane with ethyl sorbate also gave the analogous products **6** and **7**, respectively.¹²

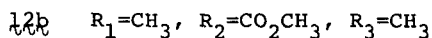
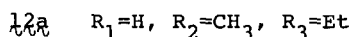
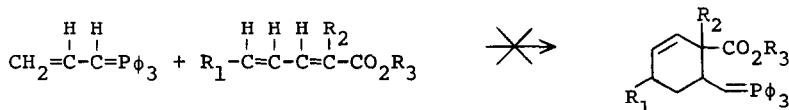


This reaction probably proceeds first by bond formation between the γ -position of the ylid and the δ -position of the ethyl sorbate to give the dipolar species **8**, which subsequently undergoes an intramolecular nucleophilic addition to the C-C double bond of the vinylphosphonium salt to give the new ylid **9**.¹³



Proton transfer then occurs to give 10 , followed by displacement of triphenylphosphine to give the norcarene 11 .

Reaction of allylidetriphenylphosphorane with ethyl 2-methyl-2,4-pentadienoate ($12a$)¹⁴ or dimethyl 2-butenylidenemalonate ($12b$),¹⁵ which no longer contain the proton α to the carboalkoxy group which is necessary for norcarene formation, does not, however, give $13a$ or $13b$. Instead, phosphonium salts were formed. These compounds have not yet been completely characterized and as in earlier reports the mechanism of their formation is uncertain.³



The conversion of ethyl sorbate via a three step sequence (ylid reaction, bromination and dehydrobromination) to the cycloheptatriene 5 in essence effects a simple three carbon 1,4-addition to an activated diene.

REFERENCES AND FOOTNOTES

- 1) This work was supported in part by Grant No. CY-04284, National Cancer Institute, U. S. Public Health Service.
- 2) National Science Foundation Predoctoral Fellow, 1971 - present.
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- 11) Spectral data compares favorably with that for ethyl 1,3,5-cycloheptatriene-1-carboxylate; G. Linstrumelle, Bull. Soc. Chim. Fr., (3), 920 (1970).
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