

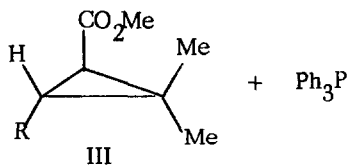
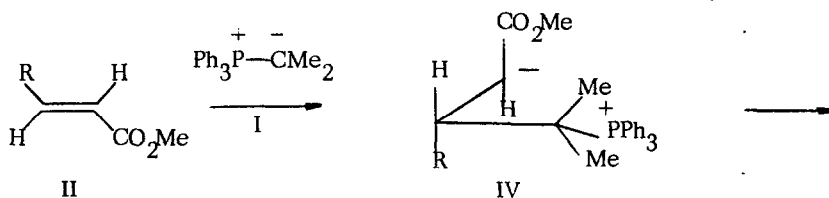
CONSTRUCTION OF THE gem-DIMETHYLCYCLOPROPANE UNIT
 EMPLOYING TRIPHENYLPHOSPHONIUM ISOPROPYLIDE

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The present communication describes an efficient route to the gem-dimethylcyclopropane unit via the 1,4 addition of triphenylphosphonium isopropylide to α,β -unsaturated esters. In their capacity as nucleophiles, alkylidene phosphoranes¹ can add to activated double bonds to form an intermediate IV which might be expected to undergo cyclopropane formation accompanied by the elimination of triphenylphosphine as indicated below:



- (a) R = \underline{m} -MeOC₆H₄-
- (b) R = CH₃CH₂CH₂CH₂-
- (c) R = \underline{m} -MeOC₆H₄CH₂CH₂-
- (d) R = CH₃CH₂CH₂CH₂CH₂-

While the conjugate addition of carbanions to α,β -unsaturated carbonyl compounds is a common reaction, only scattered reports of such additions involving alkylidene phosphoranes have been published.² A cyclopropane hydrocarbon has been reported³ from the reaction of 9-n-butylidene fluorene with n-butylidene triphenylphosphorane.

Furthermore, only two examples of an alkylidene phosphorane adding 1, 4 to an α, β -unsaturated system resulting in the formation of a cyclopropyl system have been reported.⁴ In addition, the use of triphenylphosphonium isopropylidene as a potential source of the gem-dimethylcyclopropane unit has gone unnoticed. The synthetic method described herein should be especially useful in the field of isoprenoid synthesis; for example, it should provide a simple approach to the insecticidal natural product chrysanthemic acid.

The isopropylidene transfer reaction using the ylide I and the appropriate α, β -unsaturated ester can be carried out at room temperature under nitrogen in dry THF in yields of 65-75%(distilled).⁵ Treatment of a suspension of isopropyl triphenylphosphonium iodide in THF at 25° under nitrogen with 1 equivalent of *n*-BuLi afforded a deep red solution of the ylide which after 30 minutes was treated with a THF solution of methyl-trans-oct-2-enoate(IIId). After two hours the reaction was quenched by the addition of water. Distillation afforded pure gem-dimethylcyclopropane IIIId [$\nu_{\max}(\text{CHCl}_3)$ 1715(C=O) cm^{-1} ; $\delta(\text{CCl}_4)$ 1.25 and 1.20(gem-diMe's), 3.60(s, OCH₃); mass spectrum *m/e* 198, 127(*m-71*)] in 75% yield. In addition the following cyclopropane derivatives were obtained from ylide I after distillation: IIIb(from methyl-trans-hept-2-enoate, 2 hr, 25°, 70% yield); IIIa⁶(from methyl-trans-*m*-methoxycinnamate, 4hr, 25°, 65% yield); IIIc(from methyl-5-*m*-anisyl-trans-pent-2-enoate, 2 hr, 25°, 70% yield).⁷

The synthetic method described here allows for a simple, high yield route to compounds possessing the gem-dimethylcyclopropane unit hitherto accessible by only lengthy or complicated procedures.⁸ The other known approaches to gem-dimethylcyclopropane structures appear complimentary to the route via I: replacement of bromine in gem-dibromocyclopropanes by methyl using lithium dimethylcopper⁹ and the use of the reagent from chromous salts and 2,2-dibromopropane with olefins.¹⁰

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References

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5. No attempt has been made to optimize any of the yields reported.
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