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SYNTHESIS OF TRIPHENYL-1-PHENYLTHIOVINYL PHOSPHONIUM SALTS AND USE FOR PREPARATION OF CYCLOPENTANONES

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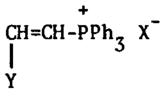
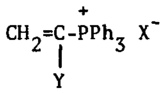
Although vinyl phosphonium salts are extremely useful in the synthesis of carbocyclic, heterocyclic and chain extended compounds,[1] those substituted in the vinyl group (general formulae I and II) do not generally react as quickly or in such high yield as does the unsubstituted compound.[2]



$\underset{Y}{CH}=CH-\overset{+}{P}Ph_3\ X^-$

I



$CH_2=\underset{Y}{C}-\overset{+}{P}Ph_3\ X^-$

II

This report describes the synthesis of the vinyl phosphonium salts II (Y = SPh, X = I, Cl or BF_4) and their use in the synthesis of cyclopentanones in high yield.

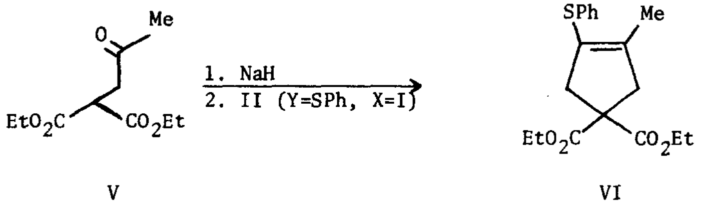
Initial attempts to prepare II (Y = SPh) by reaction between $Ph_3P=CHSPh$ and III[3] led, under a variety of conditions, only to low yields of phosphonium salts which appeared, from their NMR spectra, to be mixtures. This result was confirmed by reaction between other phosphoranes and III[4]

$CH_2=\overset{+}{N}Me_2\ Cl^-$

III

However, when either of the phosphonium salts $Ph_3\overset{+}{P}CH_2SPh\ X^-$ (X = Cl or I) was refluxed in acetonitrile with 2 equivalents of III for several days, the product obtained in about 90% yield was the desired phosphonium salt II (Y = SPh, X = Cl or I). The dimethylaminomethyl intermediate must undergo elimination under these reaction conditions.[5] The salt II (Y = SPh, X = I) is a stable colourless solid but the corresponding chloride is very hygroscopic. It may be converted to the more easily handled fluoroborate by dissolving in water and adding excess of an aqueous solution of $NaBF_4$.

The use of these substituted vinyl phosphonium salts in cyclopentanone synthesis was demonstrated by addition of the salt II (Y = SPh, X = I) to the enolate anion of the ketodiester V[6] in THF at room temperature. The desired product VI was obtained in 90% yield.[7] The vinyl thioether was readily converted to a carbonyl group by refluxing with trifluoroacetic acid in chloroform for several days.[8] The resulting ketone was purified by chromatography (yield 56%) and analysed as its DNP.



Further uses of II (Y = SPh) in synthesis are under active investigation.

References and Notes

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5. The phenylthio group plays an important part in the overall reaction since $Ph_3P^+CH_2CH_3I^-$ is recovered unchanged after prolonged reflux with III. This aspect is under further investigation.
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