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A NEW METHOD FOR THE SYNTHESIS OF OLEFINS VIA β-HYDROXY SULFOXIDES

Isao Kuwajima and Minoru Uchida

Aoyama Gakuin University, Chitosedai, Setagaya-ku, Tokyo

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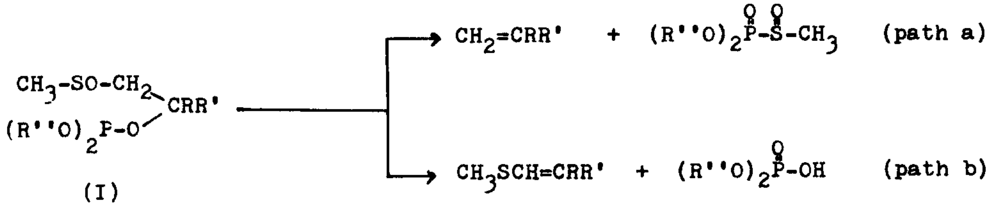
Sulfur-containing groups such as sulfide or sulfoxide are often employed to activate the neighbouring methyl or methylene group for metallation and some useful reactions have been reported.[1] However, it is also well known to be sometimes quite difficult to remove such groups after the desired reaction with an electrophile, although some efficient methods have been devised.[2]

The purpose of our present study was to establish an another method for making it easy to remove the sulfinyl group or for its conversion into an easily removable one. Trivalent phosphorus compounds are known to act as nucleophile or to have a deoxygenative effect in the reaction with the sulfoxide.[3] According to the facts, a hypothetical intermediate (I) seemed to be an interesting one to us since two types of the decomposition paths would be possible (path a; a nucleophilic attack of phosphorus to sulfur which would result in the formation of the corresponding olefin by way of elimination of methylsulfinylphosphonate[4] and

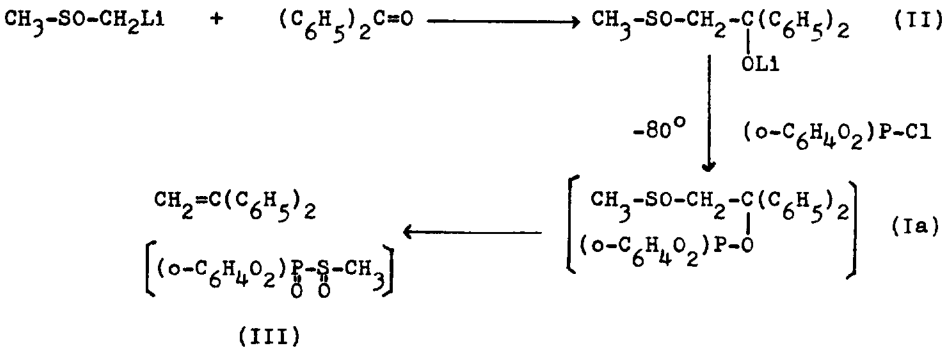


$$\mathrm{CH_3{-}SO{-}CH_2{-}CRR'{-}O{-}P(OR'')_2} \longrightarrow \mathrm{CH_2{=}CRR'} + \mathrm{(R''O)_2\overset{O}{P}{-}\overset{O}{S}{-}CH_3} \quad \text{(path a)}$$

$$\longrightarrow \mathrm{CH_3SCH{=}CRR'} + \mathrm{(R''O)_2\overset{O}{P}{-}OH} \quad \text{(path b)}$$

path b; deoxygenation reaction followed by elimination of phosphoric acid to yield methylthiovinyl ether which is known to be easily hydrolyzed to the corresponding carbonyl compound[5]), both of which would suit our above purpose.

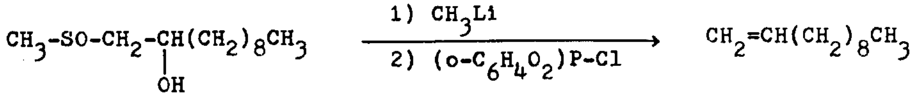
To test the possibility, preparation of (Ia; R=R'= C_6H_5, R''= o-phenylene) and its decomposition were attempted as follows; benzophenone was treated with lithio methylsulfinylcarbanion in tetrahydrofuran and to the resulting solution of (II) was added o-phenylene phosphorochloridite at -80° in situ. The red-colored solution thus obtained was gradually warmed up to room temperature and was finally heated to reflux for 1 hr, which was found to lead to the exclusive formation of 1,1-diphenylethylene (91%) along with a trace amount of 2,2-diphenyl-1-methylthioethylene. Attempt for isolation of (III) was unsuccessful probably due to its instability[6], although dialkyl ester of the similar phosphonate has been reported.[4]



By a similar procedure, (Ib; R= C_6H_5, R'= H, R''= o-phenylene) and (Ic; R= C_6H_5-CH=CH-, R'= H, R''= o-phenylene) gave the corresponding olefins, styrene and 1-phenylbutadiene in 73% and 71% yields, respectively.

Thus, it was established that the non-enolizable aldehyde or ketone could be converted efficiently into the corresponding olefin in one flask, without isolation nor purification of the intermediate.

In contrast to the successful result above, unsatisfactory result was obtained when this procedure was applied to β-hydroxy sulfoxide derived from an enolizable carbonyl compound such as n-caprinaldehyde, which gave 1-undecene in only 18% yield. This was attributable to the fact that efficient conversion into β-hydroxy sulfoxide could not be achieved by the reaction of methylsulfinylcarbanion with an enolizable carbonyl compound.[1b] Effectiveness of the reaction for removal of methylsulfinyl group was shown also in such a case by the following experiment using methyl β-hydroxyundecyl sulfoxide, isolated by tlc, as starting material. Treatment of its lithio compound with o-phenylene phosphorochloridite at -80°, followed by the similar procedure, gave 1-undecene as shown in the following equation.



$$CH_3\text{-}SO\text{-}CH_2\text{-}\underset{\substack{|\\ OH}}{C}H(CH_2)_8CH_3 \xrightarrow[2)\ (o\text{-}C_6H_4O_2)P\text{-}Cl]{1)\ CH_3Li} CH_2{=}CH(CH_2)_8CH_3$$

The results described above have suggested that the reaction proceeds predominantly via path a, but the reaction via path b can also be realized to some extent by changing the reaction condition slightly. For example, 2,2-diphenyl-1-methylthioethylene was formed in 31% yield along with 1,1-diphenylethylene (50%) when (II) was treated with o-phenylene phosphorochloridite at 0° followed by the similar procedure.

Further studies on this type of the reaction are presently being investigated.

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