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A NEW METHOD FOR THE SYNTHESIS OF OLEFINS VIA G-HYDROXYALKYL PHENYL SULFIDES

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Organo-sulfur groups such as sulfide or sulfoxide are well known to activate the neighbouring methyl or methylene group for metallation and the compound containing them has been frequently used in the synthetic organic reactions. However, a large problem how to remove such groups after an appropriate coupling reaction with an electrophile has not been dissolved completely yet. 2

In the previous paper, we reported the reaction for removal of methylsulfinyl group from  $\beta$ -hydroxyalkyl methyl sulfoxide to convert it into the corresponding clefin by way of the trivalent phosphorus compound. The purpose of our
present study was to extend this type of the reaction to removal of phenylmercapto group, which would convert  $\beta$ -hydroxyalkyl phenyl sulfide into the corresponding clefin by way of intramclecular nucleophilic attack of trivalent phosphorus to sulfur atom, followed by elimination of phenylthicl ester of phosphoric
ester as shown in the following equation. Verification of this hypothesis has

been obtained as follows.

2-Hydroxy-2,2-diphenylethyl phenyl sulfide, prepared by the reaction of phenylthiomethyllithium with benzophenone, has as converted into its phosphorous ester (Ia:  $R=R^*=C_6H_5$ ,  $R^*=0$ -phenylene) by treating its lithic alkoxide with o-phenylene phosphorochloridite at  $0^{\circ}$  in tetrahydrofuran. The resulting colorless liquid (Ia), without purification, was heated to reflux in dioxane for hr, which resulted in the formation of 1,1-diphenylethylene in 83% yield based on the hydroxy sulfide. Attempt for isolation of the corresponding phos-

phorus compound (II) was not carried out because it seemed to be unstable.

Similarly, removal of phenylmercapto group was shown to be successfully carried out in the case of the hydroxy sulfide derived from the aliphatic aldehyde and the corresponding olefin was obtained in good yield as shown in the following.

Together with the fact that both of the starting materials (A-hydroxy-alkyl phenyl sulfide and o-phenylene phosphorochloridite ) are readily available, these results have suggested that the reaction described above is expected to offer an another convenient method for preparation of terminal olefins.

Further, it was also shown that this type of the reaction was effective for removal of phenylmercapto group from g-hydroxyaldehyde diphenylthioacetal

and the corresponding phenyl vinyl sulfide was obtained in good yield by the similar procedure as shown in the following equation.

$$(C_6H_5S)_2CH-CRR^*$$
  $\xrightarrow{1) CH_3L1, 2) (o-C_6H_4O_2)P-C1}$   $\xrightarrow{C_6H_5-S-CH=CRR^*}$ 

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

$$R=R^{\circ}=C_{6}H_{5}$$
 83%

$$R_R' = -(CH_2)_5 - 68\%$$

$$R = n - C_5 H_{11}$$
,  $R' = H 79\%$ 

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