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THE REACTIONS OF α-KETOSULFIDES WITH TRIETHYL PHOSPHITE

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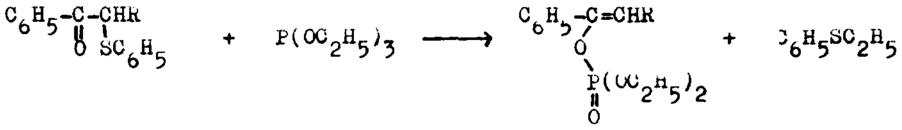
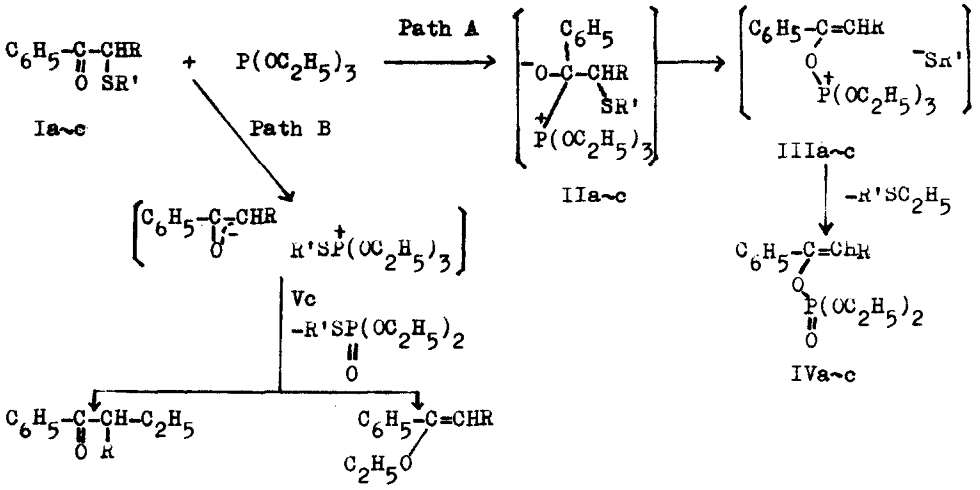
It was recently found that α-ketocarboxylates1) or α-ketotosylates2) react with triethyl phosphite to give vinyl phosphates and ethyl carboxylates or ethyl tosylates (the modified Perkow reaction).

In the present study, the reactions of α-ketosulfides with triethyl phosphite were examined with the consideration that a mercapto group would be eliminated from α-ketosulfides as an anion by the nucleophilic attack of triethyl phosphite, which results in the formation of vinyl phosphates through a quaternary phosphonium salt analogous to the case of α-ketocarboxylates or α-ketotosylates. When desyl phenyl sulfide or phenacyl phenyl sulfide were heated with triethyl phosphite at 180°C for 10 hr. under nitrogen, corresponding vinyl phosphates were obtained in 78-80% yields along with ethyl phenyl sulfide (quantitative yields), as expected. When phenacyl ethyl sulfide was treated with triethyl phosphite under the same condition, only a small amount of corresponding vinyl phosphate (ca. 6%) was obtained and almost all of the starting materials were recoverd.



R: H, C_6H_5

Next, it was established that diethyl 1,2-diphenylvinyl phosphate(27%), α-phenylbutyrophenone(15%), desoxybenzoin(13%) and 1,2-diphenylvinyl ethyl ether (18%) were obtained, when equimolar amounts of desyl ethyl sulfide and triethyl phosphite were heated at 180°C for 10 hr. under nitrogen. 1,2-Diphenylvinyl ethyl ether was identified by the reaction with dry hydrogen chloride in glacial acetic acid giving desoxybenzoin quantitatively. The infrared and nmr spectrum were in good accordance with the structure. α-Phenylbutyrophenone was confirmed by means of elemental analysis and infrared spectrum. 0,0-Diethyl-S-ethyl thiophosphate, b.p. 105-108°(10 mm),[3] and diethyl sulfide were obtained in 47% and 15% yields, respectively.



VIc

Ia: $R=C_6H_5$, $R'=C_6H_5$
Ib: $R=H$, $R'=C_6H_5$
Ic: $R=C_6H_5$, $R'=C_2H_5$

It is interesting to note that the reaction of desyl ethyl sulfide and triethyl phosphite affords both vinyl phosphate and vinyl ether[4] or ketone derivatives [4] via path A and path B, respectively, as shown in the above scheme. Path A involves a nucleophilic attack of phosphorus atom on the carbonyl carbon of α-ketosulfide to yield intermediate IIa~c, which changed to a quaternary phosphonium salt IIIa~c by an intramolecular rearrangement of phosphorus atom from carbon to oxygen accompanied with the elimination of a mercapto anion. The decomposition of the salt IIIa~c afforded vinyl phosphate and ethyl phenyl sulfide or diethyl sulfide. Path B consists of forming a quaternary phosphonium salt Vc by a nucleophilic attack of phosphorus atom on the sulfur atom of α-ketosulfide. α-Phenylbutyrophenone or 1,2-diphenylvinyl ethyl ether and 0,0-diethyl-S-ethyl thiophosphate were produced by an internal nucleophilic attack of the carbanion on the ethyl group of the salt Vc. The formation of Vc as an intermediate would be supported by the following facts: Iskander[5] reported that on treating S-desyl mercaptoacetic acid with aquaous sodium carbonate, desoxybenzoin is formed by the neutralization of a carbanion initially formed by the nucleophilic attack of hydroxide ion on the sulfur of S-desyl mercaptoacetic acid.

The formation of vinyl ether may be attributable to the great stability of phosphorus-sulfur bond, which makes the abstraction of ethyl group of the salt Vc by a reference anion, carbanion, forming vinyl ether faster than the anion exchange reaction forming the second quaternary phosphonium salt IIIc, generally known in the reactions involving quaternary phosphonium salts.

It would be noted that α-ketosulfides can react with triethyl phosphite in two ways depending on the nature of α-ketosulfides. When the mercapto group of α-ketosulfides is facile to be eliminated as an anion, such as thiophenolate group, the initial intermediate IIa~c may be readily changed to the quaternary phosphonium salt IIIa~c. Therefore, only vinyl phosphate would be resulted. On the other hand, in the case of desyl ethyl sulfide, since ethyl mercapto group is difficult to be eliminated as an anion and the desyl anion, a comparatively stable anion, is easily eliminated by the attack of the phosphite, the competitive reaction forming vinyl ether or ketone derivative through the quaternary phosphonium salt Vc would predominate over that forming vinyl phosphate.

A further study on this type of reaction is now in progress.

REFERENCES

1) T. Mukaiyama, T. Kumamoto and T. Nagaoka, Tetrahedron Letters, 1966, 5563.

2) D. B. Denney and N. Gershman, J. Org. Chem. 31, 2833 (1966).

3) b.p.120°(16 mm); P. Pistschimuka, Chem. Ber. 41, 3858 (1908).

4) Of various kinds of reactions involving a quaternary phosphonium salt, the formation of vinyl ether or ketone derivative has been proposed only in the case of reaction of hexachlorocyclopentadiene with triethyl phosphite. M. Grayson and E. J. Griffith, Topics in Phosphorus Chemistry, vol. I, p.71, Interscience Publishers, New York (1964).

5) A. Schönberg and Y. Iskander, J. Chem. Soc. 90 (1942). Y. Iskander and R. Tewfik J. Chem. Soc. 2050 (1951).