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PS - ACTIVATED ORGANOPHOSPHORUS COMPOUNDS AND THEIR USE IN OLEFIN SYNTHESIS

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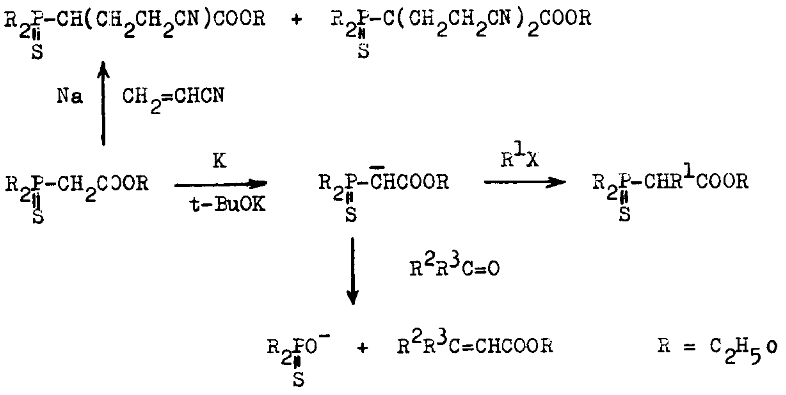
ALTHOUGH the ability of PO - group to stabilize an adjacent carbanion has been known for 37 years[1], the general importance of PO - activated organophosphorus compounds in olefin synthesis has been recognized only recently[2]. We wish to report that organophosphorus compounds can similarly be activated by PS - group.

As a model compound, ethyl diethoxyphosphinothioylacetate (I), prepared by Michaelis-Becker reaction from sodium diethylthiophosphite, was used. The potassium derivative of (I), obtained by action of the metal in boiling benzene was alkylated under standard conditions[1]. The Michael addition of acrylonitrile gave rise to formation of mono and bis cyanoethylated products[3]. The phosphonothionate anion for olefin synthesis was generated either by the action of metallic potassium or potassium t-butoxide in refluxing benzene. Benzaldehyde in the presence of potassium t-butoxide in boiling benzene gave potassium diethylphosphorothioate, identified as the free acid, and crude ethyl cinnamate[4] converted by alkaline hydrolysis into cinnamic acid (m.p. 130-132°, 85% yield). The procedure in which potassium metal was applied was less satisfactory and cinnamic acid obtained in 50% yield. Similar reaction with m-nitrobenzaldehyde gave ethyl m-nitrocinnamate (m.p. 73-75°, 47% yield) characterized as the acid (m.p. 203-204°) and with benzophenone gave 2,2-diphenylacrylic acid (m.p. 159-161°, 30% yield).



It is interesting to note that whereas the phosphorothionate anion is formed more slowly than the phosphonate, due to the expected decreased acidity of the methylene group in (I), their reaction with aldehydes and ketones appears to proceed similarly. The process involves undoubtedly addition of the anion derived from (I) to the carbonyl group followed by elimination of the stable anion $R_2P(S)O^-$ to yield the olefin. It is hoped to gain a somewhat more intimate view of the reaction by using optically active phosphinothioates containing an asymmetric phosphorus atom.

REFERENCES

1. A. E. Arbuzov and A. A. Dunin, Ber.dtsch.chem.Ges. **60**, 291 (1927).
2. Cf., S. Trippett, Quart. Rev. (London) **17**, 431 - 434 (1963).
3. B. Fiszer and J. Michalski, Roczniki Chem. **26**, (1952); **28**, 185 (1954).
4. The isolation of neutral reaction products in all cases described is somewhat more difficult than in the case of the PO - compound.