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Synthesis and Reactivity of Unsaturated Bisphosphonium Salts

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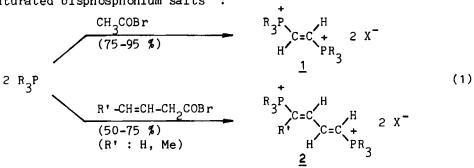
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SYNTHESIS AND REACTIVITY OF UNSATURATED BISPHOSPHONIUM SALTS

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Abstract The synthesis of 1,2 vinylene bisphosphonium salts 1 has now been enlarged to the vinylogous 1,4-butadienylene bisphosphonium salts 2. The salts 2, a new class of unsaturated disalts, have also been prepared through a two-step isomerisation of acetylenic salts. New aspects of the reactivity of salts 1 and the comparative study of salts 2 (selective cleavage reactions of P-C bonds and reactions with nucleophiles having a mobile hydrogen) are described. This reactivity allows the preparation of new series of phosphonium salts substituted by hetercatomic groups.

In an earlier study, the reaction of tertiary phosphines with acetyl bromide has afforded a new synthesis of 1,2 vinylene bisphosphonium salts $\underline{1}$. We have now been able to enlarge through vinylogy this synthesis to the preparation of the higher homologs, the 1,4-butadienylene bisphosphonium salts $\underline{2}$, which are a new class of unsaturated bisphosphonium salts²:

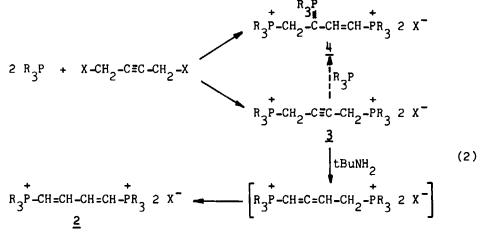


$$^{R}_{3}^{P}$$
: $^{PhPMe}_{2}$, $^{Ph}_{2}^{PMe}$, $^{Ph}_{2}^{PCH}_{2}^{Ph}$, $^{Ph}_{2}^{PCH}_{2}^{CH}_{4}^{CH}_{2}^{CH}$, $^{Ph}_{2}^{PCH}_{2}^{CH}_{2}^$

It must be pointed out that only one isomer with the E or E,E stereochemistry, is obtained in this reaction.

The same salts $\underline{2}$ can also be prepared by two successive isomerisations (propargyl-allenyl, then allyl-vinyl isomerisation) starting from acetylenic disalt $\underline{3}$ in the presence of bases like tBuNH₂ (Equation (2)).

During the preparation of disalt $\underline{3}$ according to the literature³, we have observed the formation of a side-product, the structure of which could be determinated unequivocally as the ylidedisalt $\underline{4}$; but, changing the dihalogenide, the reaction can be controlled to give selectively either the compound $\underline{3}$ or the compound $\underline{4}$.



The compounds $\underline{1}$ and $\underline{2}$ contain an unsaturated bridge (a new kind of structure in the case of salts $\underline{2}$) whose UV-spectroscopic characteristics show a strong $d\pi$ - $p\pi$ interaction with both phosphorus atoms; this interaction involves a notable reactivity of the bridge: decrease in the activity of the π -system towards partners for Diels-Alder reaction, but, on the contrary, high reactivity towards nucleophilic agents.

Particularly, with the disalts 1 or 2, in which the phosphorus bears a labile benzyl, cyano-2-ethyl or allyl group, the LiAlH₄, alkaline alcoolates or cyanides cleavage reaction affords one or two tertiary phosphines according only to the selective cleavage of the

unsaturated bridge between the two phosphorus atoms. The 1,2-vinylene bridge, particularly, includes a P-C bond which is till now among the most easy to cleave in the chemistry of phosphonium salts.

Towards nucleophilic agents bearing a mobile hydrogen ZH the disalts 1 and 2 behave differently, in basic medium, because of the greater instability of the unsaturated bridge for compound 1. Starting from disalt 1, we have recently shown⁵ that the reaction involves really the formation of an intermediate, the ethynylphosphonium salt $\underline{5}$, which accounts for the various end-products (the exact nature of the reagent ZH determines actually the reaction path-way to the phosphoniovinylation product $\underline{6}$, to the phosphonioethylation product $\underline{7}$ or to various secondary products like compound $\underline{8}^5$):

ZH : ROH, ArOH, RSH, ArSH, Ar2PH, RNH2, R-CH=N-OH

At the opposite, the disalts $\underline{2}$ react essentially as bis(vinyl-phosphonium)salts and give a double addition of compounds ZH (Equation (5)):

$$Ph_{3}P-CH=CH-CH=CH-PPh_{3} 2 Br^{-} HZ ZH ZH ZH PPh_{3} 2 Br^{-} (5)$$
 HZ
 $ZH: HO(CH_{2})_{n}OH, H_{2}N(CH_{2})_{n}NH_{2}$

It has already been shown that salts $\underline{6}$ are very good vinylation agents for alcohols and phenols⁶, while salts $\underline{7}$ give suitable Wittig's reagents for the n+1 homologation of aldehydes⁷. Salts $\underline{9}$ ought to be also useful for organic synthesis.

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