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EVIDENCE FOR THE FORMATION OF A γ-REARRANGED ALLYLIC PHOSPHONIUM SALT

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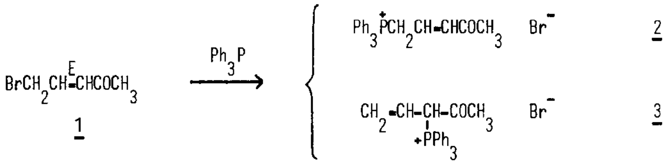
Although the conversion of α-halogenoketones to phosphonium salts is well documented[1], nothing is known about similar transformations in γ-halogeno-α,β-unsaturated ketones, e.g. (E)-5-bromo-3-penten-2-one, 1.

Enriched crudes of 1 react satisfactorily with Ph_3P. These crudes can be obtained either by allylic bromination of pure (preparative g.l.c.) (E)-3-penten-2-one[2] or by Wittig condensation of bromoacetaldehyde[3] and acetylmethylenetriphenylphosphorane. A mixture of two isomeric phosphonium salts (correct elemental analysis) is produced in the reaction of 1 with Ph_3P, as seen by n.m.r.:

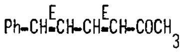


$$\underset{1}{BrCH_2CH\overset{E}{=}CHCOCH_3} \xrightarrow{Ph_3P} \begin{cases} Ph_3\overset{+}{P}CH_2CH{=}CHCOCH_3 \quad Br^- & 2 \\ CH_2{=}CH{-}\underset{+PPh_3}{CH}{-}COCH_3 \quad Br^- & 3 \end{cases}$$

Scheme 1

4-oxo-2-pentenyltriphenylphosphonium bromide, 2, (δ=2.2, CH_3; 6.8, CH=CH) and 1-vinyl-2-oxopropyltriphenylphosphonium bromide, 3, (δ=2.3, CH_3; 4.3, $=CH_2$) in a 3:1 ratio.

Treatment of this mixture of phosphonium salts with t-BuOK and condensation with benzaldehyde afforded a t.l.c. separable mixture of (3E,5E)-6-phenyl-3,5-hexadien-2-one[4], 4, and (Z)-3-benzylidene-4-penten-2-one, 5, [δ=2.45 (3H,s); 5.4 (2H, J_{13}=18 Hz, J_{23}=11 Hz and J_{12}=2 Hz); 6.5 (1H, J_{31}=18 Hz and J_{32}=11 Hz); 7.3 (1H,s); 7.47 (5H,s)] in the same ratio of the original salts (3:1).



$$Ph{-}CH\overset{E}{=}CH{-}CH\overset{E}{=}CH{-}COCH_3$$

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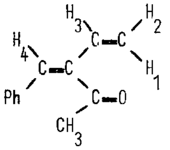

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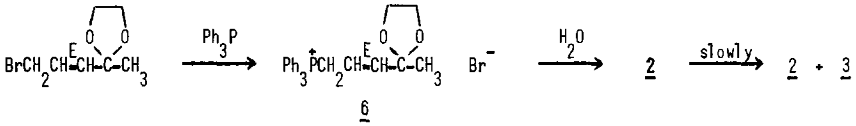
This is the first time that in the reaction between an allyl bromide derivative and Ph_3P both possible phosphonium salts, i.e. "normal" and "rearranged" have been detected.

γ-Condensation of an allylic phosphonium bromide has been described by Corey and Erickson[5] in the condensation of the phosphorane derivative from pure (n.m.r.) (E)-3-methoxy-2-methylallyltriphenylphosphonium bromide with n-hexanal giving methyl 2-isopropenyl-2-octenoate along with the α-condensation products.

One of the three paths proposed by Corey to explain this γ-condensation involves allylic rearrangement of Ph_3P group before normal Wittig condensation, although the rearranged phosphonium salt was actually never observed. On the other hand, Castells et al.[6] had previously described a similar condensation between the phosphorane from 4-bromo-3-methyl-2-butenal and 4-nitrobenzaldehyde assuming that the salt was the rearranged one, since only 3-(4-nitrophenyl)-2-isopropenyl-2-propenal was isolated. No n.m.r. of the salt could be run. Our finding supports previous rearrangement of the allylic phosphonium bromides. This rearrangement should depend on the electron-withdrawing character of the carbonyl group ($CHO > COCH_3 > COOCH_3$).

Moreover, in the reaction between (E)-5-bromo-3-penten-2-one ethyleneketal and Ph_3P we have always obtained a pure salt, the normal one, (E)-4,4-ethylenedioxi-2-pentenyltriphenylphosphonium bromide, 6, (correct elemental analysis):



Hydrolysis of 6 gives pure 2, that in ethereal suspension very slowly converts into a mixture (3:1) of 2 and 3. This fact and the reaction of Scheme 1 suggest two possible mechanisms:

i) a mechanism implying formation of 2 by a S_N2 attack of Ph_3P and subsequent partial rearrangement of 2 into 3.

ii) the possibility that both salts are formed simultaneously from the collapse of the intermediate $Ph_3\overset{+}{P}Br$ $^{-}CH_2CH{=}CHCOCH_3$ arising from the nucleophilic attack of Ph_3P to the halogen atom[7].

References

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