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PHOSPHONIUM SALTS FROM γ-BROMO-α,β-UNSATURATED ALDEHYDES. CONDENSATIONS OF THE CORRESPONDING "YLIDALS". 1,2,5,6-DIBENZOCYCLOOCTATETRAENE

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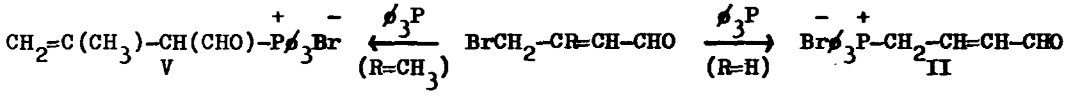
Reaction of trans-γ-bromocrotonaldehyde (I) (1) with triphenylphosphine, in ether solution afforded (76% yield of crude product (2)) (3-formylallyl)-triphenylphosphonium bromide (II) (m.p. 175-7(d); IR(KBr): 2760, 1640, 995cm^{-1}; NMR(CDCl$_3$): 0,56(d, J=7Hz), 4,70(CH$_2$, q, J_{HP}=16Hz, J_{HH}=7Hz)), which was converted into the "ylidal" (3) (3-formylallyliden)-triphenylphosphorane (III) (orange, unstable crystals, m.p. 153-5; IR(KBr): 1605, 1543, 873 cm^{-1}), by treatment of its aqueous solution with an equimolecular amount of aqueous sodium hydroxide, and simultaneous extraction with methylene chloride. Alternatively, the phosphonium salt (II) was dehydrobrominated to (III) by passing its chloroform solution through an alkaline alumina column (4, 5).

Reaction of p-nitrobenzaldehyde with the "ylidal" (III) gave the known 5-(p-nitrophenyl)-penta-2,4-dienal (6) (12% yield).

In contrast to the behaviour of γ-bromocrotonaldehyde, γ-bromo-β-methylcrotonaldehyde (IV) (cis-trans (1:3) mixture) (1) reacted with triphenylphosphine to give the allylic rearranged salt, (1-formyl-2-methylallyl)-triphenylphosphonium bromide (V) (m.p. 205-12 (d), IR(KBr): 1668, 898 cm^{-1}); this was dehydrobrominated in aqueous solution to the corresponding "ylidal", (1-formyl-2-methylallyliden)-triphenylphosphorane (VI) (IR(KBr): ca. 1575 cm^{-1}).

Reaction of p-nitrobenzaldehyde with the "ylidal" (VI) gave (89% yield) 3-(p-nitrophenyl)-2-isopropenylprop-2-enal (VII) as a cis-trans (1:20) mixture (NMR monitoring); column chromatography afforded the pure trans-isomer (m.p. 78-81; IR(CCl$_4$): 1700, 1600, 1528, 1374, 910 cm^{-1}; NMR(CCl$_4$): 0,5(s), AA'BB' pattern centered at 1,74 and 2,26, J=9Hz, 2,88(s), 4,72 and 5,10(terminal CH$_2$), and 8,08(s)).



$$\underset{\text{V}}{CH_2{=}C(CH_3){-}CH(CHO){-}\overset{+}{P}\phi_3\overset{-}{Br}} \xleftarrow[(R=CH_3)]{\phi_3P} BrCH_2{-}CR{=}CH{-}CHO \xrightarrow[(R=H)]{\phi_3P} \underset{\text{II}}{\overset{-}{Br}\phi_3\overset{+}{P}{-}CH_2{-}CH{=}CH{-}CHO}$$

Reaction of *o*-diacetoxymethylbenzyl bromide (VIII)(7) with triphenylphosphine gave (77% yield) the corresponding salt, triphenyl-(*o*-diacetoxymethylbenzyl)-phosphonium bromide (IX) (m.p. 206-16(d); IR(KBr): 1760, 1743 cm^{-1}; NMR($CDCl_3$): 1,9-2,9(m), 4,49(d, J_{HP}=15Hz), 8,08(s)) from which triphenyl-(*o*-formylbenzyl)-phosphonium bromide (X) (m.p. 261-72(d); IR(KBr): 2858, 2825, 2768, 1675 cm^{-1}; NMR($CDCl_3$): 0,6(s), 2,1-2,7(m), 4,17(d, J_{HP}=16Hz), was obtained in high yield (86%) by refluxing in dilute aqueous hydrobromic acid. This salt is interesting in that the corresponding "ylidal" (XI) will have the two reactive centers in a *cis*-relationship, and this should make possible an intramolecular Wittig reaction; however attempts in this direction were unsuccessful.

Coupling of two molecules of "ylidal" (XI) could lead to dibenzocyclooctatetraene (XII) if the double bond first formed had a *cis*-stereochemistry; with this in mind, a dehydrobromination of the phosphonium salt (X) was performed with lithium ethoxide in DMF (8). The resulting reaction mixture was very complex (at least nine compounds present) but from it, pure (t.l.c.) 1,2,5,6-dibenzocyclooctatetraene (8) (m.p. 107-9; IR(CCl_4): 3060, 3008, 1496 cm^{-1}; NMR (CCl_4): 2,97(s, 8H), 3,33(s, 4H)) was isolated in *ca*. 6% yield.

Compounds (II), (III), (V), (VII), (VIII), (IX), and (X) gave satisfactory elemental analysis.

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7.- This compound was prepared by the sequence: *o*-tolualdehyde $\xrightarrow{1}$ *o*-diacetoxymethyltoluene $\xrightarrow{2}$ *o*-diacetoxymethylbenzyl bromide. 1.- acetic anhydride, H^+. 2.- NBS in CCl_4.
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