ω-BROMOALKAPOLYENYLMETHYL KETONES—I

REACTION OF 5-BROMO-3-PENTEN-2-ONE WITH TRIPHENYLPHOSPHINE

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Abstract—The reaction of (E)-5-bromo-3-penten-2-one with triphenylphosphine affords a 3:1 mixture of two protomeric phosphonium salts: 4-oxo-2-pentenyltriphenylphosphonium bromide and 4-oxo-1-pentenyltriphenyl-phosphonium bromide, characterized by the ^{13}C NMR spectrum of the mixture. However, the common phosphorane of these salts gives two condensation products with benzaldehyde, corresponding to α- and γ-condensation respectively.

In recent years we have conducted several approaches to the syntheses of ω-halogenopolyenic esters of the type 1, which are interesting synthetic intermediates through their conversion to phosphonium salts or phosphonates.[1] Nevertheless, the usefulness of α,ω-difunctional polyenes is reinforced in those derivatives that possess methyl substituents in appropriate positions, e.g. derivatives of the type 2, because they can be considered as good isoprenoid synthons.

$$X–CH_2–(CH=CH)_n–COOCH_3$$
1

$$X–CH_2–(CH=CH–C=CH)_n–COOCH_3$$
$$\underset{CH_3}{|}$$
2
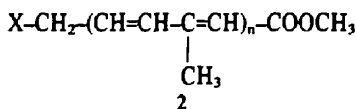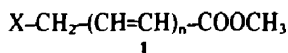
Compounds of these characteristics could be, and actually have been, utilized through their phosphonium salts or phosphonates in the syntheses of carotenoids.

A structural analysis of the carotenoid molecules lead us to consider synthons C₅ as their building blocks. On Table 1 a list is set of different C₅-synthons described in the literature,[2] neither of which proceeds from a double disconnection of methyl substituted olefinic bonds. Such a disconnection would give us the C₅-synthon 5-halogeno-3-penten-2-one 3, or in general ω-halogenoalkapolyenylmethyl ketones of the type 4 (Fig. 1).

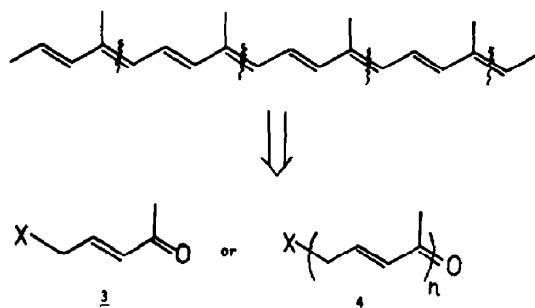Since no Wittig or Wittig–Horner condensations of 4

Fig. 1.

were known (for $n \geq 1$), we decided to explore their applicability into the construction of carotenoid molecules. The C₅-synthon 3 (in form of its phosphonium salt or phosphonate) should be the "ideal" isoprenoid unit in a series of iterative Wittig-like reactions.

(E)-5-Bromo-3-penten-2-one (3; X = Br). For different reasons, but mainly for synthetic simplicity, the halogen employed in the C₅-synthon 4, n = 1, was bromine, (3; X = Br) being 5-bromo-3-penten-2-one the first target of our work.

The synthesis of 3, X = Br, can be accomplished, as indicated by Awang and Vincent,[3] by allylic bromination of (E)-3-penten-2-one with N-bromosuccinimide; these authors showed in contrast with a previous work[4] that the bromination proceeds into the allylic rather than into the α-position of the ketone. We have confirmed this, but we have also observed that the reaction is not clean, giving side-products that cannot be purified by distillation due to the decomposition of, 3, X = Br, and that cannot produce directly a crystalline phosphonium salt in their reaction with triphenylphosphine.

We have obtained (E)-5-bromo-3-penten-2-one, which can be converted into a crystalline phosphonium salt, by any of the following procedures:

(i) Allylic bromination of *pure* (E)-3-penten-2-one. This commercial ketone contains ca. 20% of mesityl oxide, that must be separated by preparative GLC or by spinning-band distillation. Moreover, the bromination with NBS must be carried out in the presence of sodium hydrogen carbonate and calcium oxide,[5] the yield of brominated product being very sensitive to irradiation times. The presence of the solid bases should scavenger

Table 1.

Ph₃⁺PCH₂C=CHCOOCH₃ Br⁻ 　　　　　| 　　　　　CH₃	Ph₃⁺PCH₂CH=CCOOCH₃ Br⁻ 　　　　　　　| 　　　　　　　CH₃
(EtO)₂PCH₂C=CHCOOCH₃ 　　　　‖　| 　　　　O　CH₃	(EtO)₂PCH₂CH=CCOOCH₃ 　　　　‖　　　| 　　　　O　　　CH₃
Ph₃⁺PCH₂C=CHCH(OEt)₂ Br⁻ 　　　　　| 　　　　　CH₃	Ph₃⁺PCH₂CH=CCHO Cl⁻ 　　　　　　　| 　　　　　　　CH₃
	(EtO)₂PCH₂CH=CCH(OEt)₂ 　　　　‖　　　| 　　　　O　　　CH₃

off the formed hydrogen bromide that presumably promote polymerization of the highly reactive bromounsaturated ketone.

(ii) Wittig condensation of bromoacetaldehyde[6] with methylcarbonylmethylenetriphenylphosphorane. This approach gives, 3, X = Br, in moderately pure form. The ^{1}H NMR spectrum of the bromopentenone 3, X = Br, shows the E configurations of the double bond as an AB system centered at δ 6.4 with J_{AB} = 16 Hz.

Reaction of (E)-5-bromo-3-penten-2-one with triphenylphosphine; the problem of the constitution of the formed phosphonium salt.

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

Moderately pure, 3, X = Br, reacted satisfactorily with triphenylphosphine to give a crystalline product, m.p. 183–186°, that analyzed correctly for $C_{23}H_{22}BrOP$, but the product was shown to be a mixture of at least two salts by its ^{1}H NMR spectrum. On a previous communication[7] we claimed this mixture to be formed by 4-oxo-2-pentenyltriphenylphosphonium bromide, 5-Br, and 1-vinyl-2-oxopropyltriphenylphosphonium bromide, 6, in a ratio 3:1.

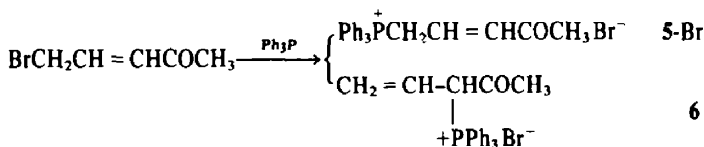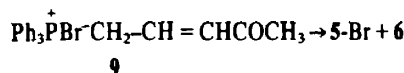through 4-bromo-3-methyl-2-butenal. Out of the three mechanisms proposed by Corey to explain its γ-condensation products, two involved allylic rearrangement of the triphenylphosphorus moiety, one prior to the formation of the ylide, i.e. migration of the moiety into the phosphonium salt.

This migration seemed to us the most attractive mechanism for our unbranched (5-Br and 6) phosphonium salts, since we could detect initially two salts, suggesting two possible paths to arrive at this mixture:

(i) S_N2 attack of triphenylphosphine to 3, X = Br, and subsequent partial rearrangement of 5-Br to 6.

$$Ph_3\overset{+}{P}CH_2CH = CHCOCH_3\,Br^- \rightleftarrows CH_2 = CH\text{--}CHCOCH_3$$
$$|$$
$$+PPh_3\,Br^-$$

5-Br   6
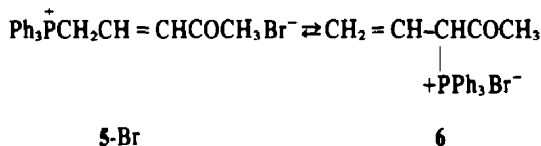
(ii) Simultaneous formation of both salts from the collapse of the intermediate 9 arising from the nucleophilic attack of triphenylphosphine to the halogen atom:[10]

$$Ph_3\overset{+}{P}Br^-CH_2\text{--}CH = CHCOCH_3 \rightarrow \text{5-Br} + 6$$
9

$$BrCH_2CH = CHCOCH_3 \xrightarrow{Ph_3P} \begin{cases} Ph_3\overset{+}{P}CH_2CH = CHCOCH_3\,Br^- \quad \text{5-Br} \\ \\ CH_2 = CH\text{--}CHCOCH_3 \\ \qquad\qquad | \qquad\qquad\qquad 6 \\ \qquad\quad +PPh_3\,Br^- \end{cases}$$

We based this assumption in the following facts:

(i) The signals present in the ^{1}H NMR spectrum; δ 2.2 (–CH$_3$) and δ 6.8 (–CH=CH–) that should correspond to the salt 5-Br and δ 2.3 (–CH$_3$) and δ 4.3 (=CH$_2$) that could correspond to the salt 6.

(ii) The condensation with benzaldehyde of the ylides generated from the inseparable mixture of phosphonium salts; from the final crude we could separate and identify $(3E, 5E)$-6-phenyl-3,5-hexadien-2-one, 7, and (Z)-3-benzylidene-4-penten-2-one, 8, in the same ratio as the presumed original salts.
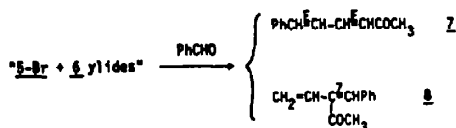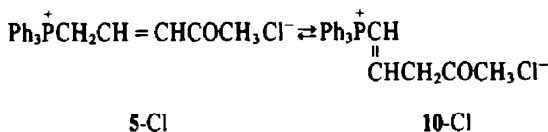

Fig. 2.

Aldehydes normally condense with allylic phosphonium ylides at the ylid α-carbon atom. Only one case is reported[8] in which a well characterized methyl-branched allylic phosphonium ylide {(E)-3-methoxycarbonyl-2-methylallyltriphenylphosponium bromide} generates the normal α-condensation product and/or the γ-condensation one under the appropriate conditions. A γ-condensation was already reported[9] for another not as well documented branched phosphonium ylide formed

However, against these assumptions exists the claim by Zbiral,[11] who reported the preparation of a mixture of 4-oxo-2-pentenyltriphenylphosphonium chloride, 5-Cl, and its proton tautomer 4-oxo-1-pentenyltriphenylphosphonium chloride, 10-Cl, from allylidenetriphenylphosphorane and acetyl chloride. The ^{1}H NMR spectrum of both mixtures of salts, Zbiral's and ours, were identical.

$$Ph_3\overset{+}{P}CH_2CH = CHCOCH_3\,Cl^- \rightleftarrows Ph_3\overset{+}{P}CH$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\overset{\parallel}{C}HCH_2COCH_3\,Cl^-$$

5-Cl   10-Cl

Since neither ^{1}H NMR spectrum could decide for the mixture 5–6 or 5–10 nor could do it the fact of γ-condensation (two mechanisms not implying prior rearrangement of the salt 5 can explain, according to Corey,[8] for the γ-condensation product) a ^{13}C NMR spectrum (Fig. 3) of the salts mixture was run.

From the pattern of this spectrum and from the off-resonance spectrum we can conclude that the mixture is composed mainly by (E)-4-oxo-2-pentenyltriphenylphosphonium bromide, 5-Br, and (E)-4-oxo-1-pentenyltriphenylosphonium bromide, 10-Br. We base this asseveration on the study of the following regions of the spectrum:
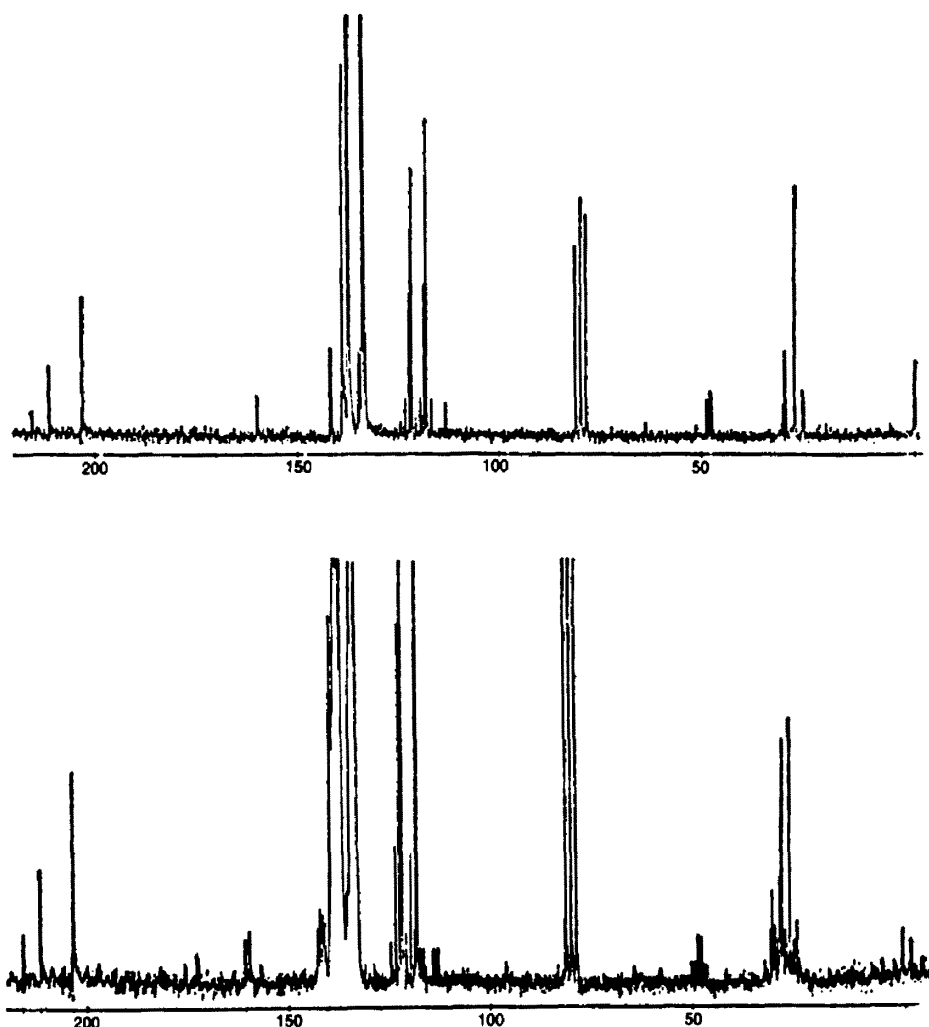
(i) Carbonyl region. Three signals are observed at

Fig. 3.

207.84, 203.99 and 196.30 ppm. The more shielded one should correspond to a conjugated carbonyl, i.e. to the carbonyl of the salt 5-Br (compare with the position of the carbonyl carbon of butenone,[12] 198.1 ppm), while signals at 204 and 208 ppm should correspond to non conjugated ketones, most probably the signal at 204 ppm to the carbonyl of the salt 10-Br (compare with the position of the carbonyl carbon of butanone,[12] 206.3 ppm) and the signal at 208 ppm to a third unidentified phosphonium salt.

(ii) Olefinic region of vinylic and allylic phosphonium salts. Freeman et al.[13] have studied the chemical shifts and the ^{31}P-^{13}C coupling constants of vinylic and allylic phosphonium salts. Table 2 gives some of the parameters observed by these authors.

β-Carbon atoms in vinylic phosphonium salts appear always cleanly differentiated (deshielded) from others olefinic carbons due to $d\pi$-$p\pi$ bonding and with a very small J_{CP}. In this region (156.04 ppm) we have a doublet ($J \simeq 3$ Hz), that can be assigned to the β-carbon atom of the vinylic phosphonium salt 10-Br. In the off-resonance spectrum this signal appears as a doublet of doublets. Moreover, at 112.6 ppm another doublet ($J_{CP} = 82.1$ Hz) is encountered, that could be assigned to the α-carbon atom of the same salt. The off-resonance spectrum gives this signal as a doublet of doublets.

Bands corresponding to the olefinic carbon atoms of salt 5-Br must be masked by the benzenic carbon atoms (129–135 ppm).

(iii) Region of the ipso-carbon atoms of triphenyl-

Table 2.

Compound	Carbon chemical shifts, ppm			^{31}P-^{13}C coupling constants, Hz		
	[1]	[2]	[3]	[1]	[2]	[3]
$Ph_3\overset{+}{P}$-CH=CH$_2$ X$^-$	119.2	145.2		80.3	0	
$Ph_3\overset{+}{P}$-CH=CHCH$_3$ X$^-$	110.1	159.5	21.7	86.1	2.6	19.9
$Ph_3\overset{+}{P}$-CH$_2$CH=CH$_2$ X$^-$	28.6	126.3	123.1	49.7	13.4	9.8

phosphonium salts. The chemical shifts of the *ipso*-carbon atom in phosphonium salts has also been studied by Freeman[13] and found to be very constant (119.4–117.1 ppm) with coupling constant of 90 Hz for vinylic and 86 Hz for allylic phosphonium salts.

Among other small signals in our spectrum we can identify two doublets (not further resolved in the off-resonance spectrum), one centered at 117 ppm with $J_{CP} = 85.7$ Hz and other centred at 117.5 ppm (less intense) with $J_{CP} = 92$ Hz. These signals have to be correlated with ipso-carbon atoms of phosphonium salt 5-Br and 10-Br respectively.

(iv) Methylene and methyl region. A signal at 48 ppm (doublet $J_{CP} = 19$ Hz; two triplets in off-resonance) is assigned to the methylene of the salt 10-Br. Signals at 30.4 and 28.2 ppm correspond to the methyl groups in salts 10-Br and 5-Br respectively (quartets in off-resonance). Finally, the more shielded signal at 26.3 ppm is part of the doublet of the methylene of the salt 5-Br ($J_{CP} = 47.9$ Hz), the second band being beneath the signal at 28.2 ppm: the off-resonance spectrum resolves all the bands showing the presence of the two triplets corresponding to this methylene.

A third, non conjugated salt, seems to be present in very small proportion, but the bulk of the mixture is composed, as Zbiral proposed, by the salts 5-Br and 10-Br. This fact forces us to choose some of the other two alternative mechanisms proposed by Corey[8] to explain the γ-condensation of the unique ylide formed from the mixture of the two salts. Scheme 1 gives the

Scheme 1.

possible paths of the unprecedented γ-condensation of an unbranched ylide, which is also the first reported condensation of a γ-phosphonium ylide of an α,β-unsaturated ketone.

Utilization of the C_5-synthon (3; X = Br)

Although, 3, X = Br, reacts with triphenylphosphine giving two protomeric phosphonium salts, the corresponding ylide is common and condenses easily with aldehydes. With benzaldehyde gives (3E,5E)-6-phenyl-3,5-hexadien-2-one,[14] 7, identified by its ¹H NMR spectrum run in the presence of Eu(fod)₃: the addition of 0.17 equivalents of this lanthanide complex permits the identification of H_α (doublet, J = 15 Hz) and H_β (doublet of doublets, $J_{\alpha\beta} = 15$ Hz, $J_{\beta\gamma} = 9$ Hz), while the addition of 0.375 equivalents resolves the system H_γ–H_δ: a doublet of doublets for $H_\gamma (J_{\gamma\delta} = 15$ Hz) and a doublet for H_δ. Every one of these protons were assigned by the slopes of the plot of the induced chemical shifts vs the equivalents of Eu(fod)₃ added.
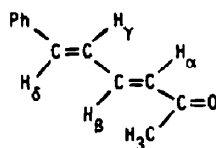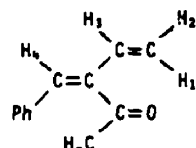
In the same reaction an oil can be separated identified by its ¹H NMR spectrum as (Z)-3-benzylidene-4-penten-2-one 8, since it presents a methylenic system (H₁–H₂) completely analogous to that of styrene at δ 5.4; H₃ appears as a doublet of doublets, δ 6.5 $J_{31} = 18$ Hz and $J_{32} = 11$ Hz and H₄ absorbs as a singlet at δ 7.3. The very low downfield chemical shift of the methyl group (δ 2.45) must be caused by the paramagnetic effect of the phenyl group and is this data that forces us to admit the Z configuration for the double bond.

With 4-nitrobenzaldehyde the common ylide 11 gives stereoisomeric mixtures of (3E, 5Z-E)-6-(4-nitrophenyl)-3,5-hexadien-2-one,[15] 12, γ-condensation product not being detected. The major product, the isomer (3E,5E)-12, was identified by its ¹H NMR spectrum analogous, but downfield shifted, to the spectrum of 7.

Unfortunately the ylide 11 did not condense with acetone or other ketones, not allowing its use as an iterative C_5-synthon in carotenoid syntheses. To obviate this problem we have tried, without success, to convert the bromopentenone (3; X = Br) to the corresponding phosphonate (13; R = Me, Et).
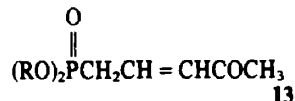
$$(RO)_2 \overset{\displaystyle O}{\overset{\displaystyle \|}{P}} CH_2CH = CHCOCH_3$$
$$\mathbf{13}$$

The difficulties encountered in the Arbuzov reaction of α-halogenoketones are well known:[16] the enol phosphate is many times the final product instead of the normal phosphonate. Moreover, as far as we know, no Arbuzov reactions have been described on γ-halogeno-α,β-unsaturated ketones.

Since the presence of the carbonyl group in the investigated C_5-synthon might cause the poor reactivity of the phosphonium ylide and the abnormal Arbuzov reaction, preventing the preparation of the phosphonate,
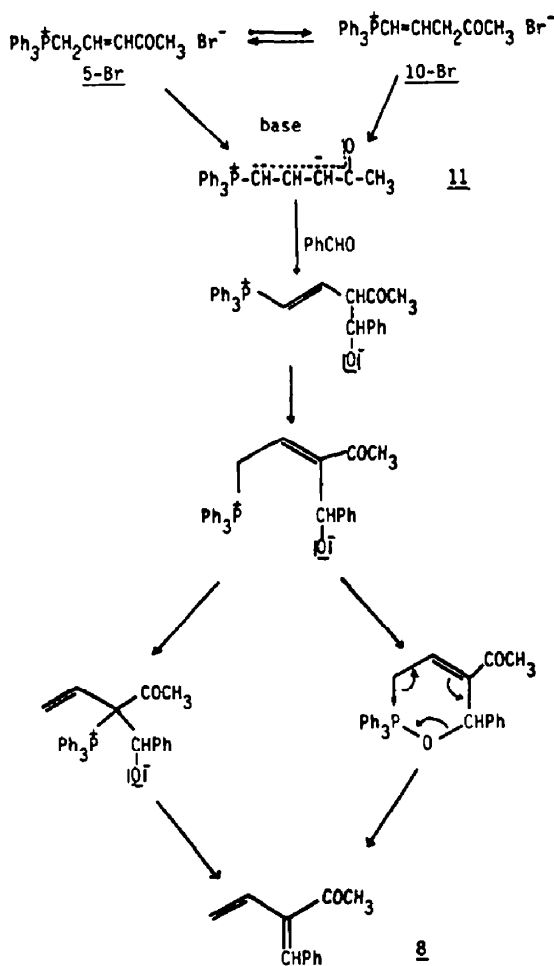
further research has been done in order to protect the carbonyl group, and this is reported in the following paper (Part II).

EXPERIMENTAL

^{1}H NMR spectra were recorded in CDCl$_3$ (TMS as an internal standard) on a Perkin–Elmer R-12 spectrometer (60 MHz). ^{13}C NMR spectra were recorded in CDCl$_3$ (TMS) on a Varian XL-100 spectrometer.

Methylcarbonylmethyltriphenylphosphonium chloride. The product is described by Ramirez and Dershowitz.[17] We obtained it by refluxing one hour a concentrated chloroform solution of dried triphenylphosphine and chloropropanone and precipitating the phosphonium salt with hexane. Yield 92%. m.p. 228–236° (lit. 237–238°).

Methylcarbonylmethylenetriphenylphosphorane **14**. Although this product has been described,[17] we prepared it by an alternative route.

65.0 g (0.184 mol) of methylcarbonylmethyltriphenylphosphonium chloride were dissolved in 1.8 l of water. While the solution was stirred 1N NaOH was dropwise added until the pH reached the value 7–8 (185 ml). The precipitate was filtered, washed with water until neutral and dried first over KOH and then over P$_2$O$_5$ to constant weight. Yield 56.6 g (0.178 mol; 97%) of phosphorane **14**. m.p. 206–208° (lit. 205–206°).

(E)-3-penten-2-one. This ketone was prepared as described by House *et al.*[18] with the modification that the solution of the phosphorane was cooled in an ice-bath during the addition of acetaldehyde. The yield in pure (E)-3-penten-2-one was 89%. Commercial (E)-3-penten-2-one (Aldrich) was found to contain 20% 4-methyl-3-penten-2-one. Both ketones were purified by preparative GLC on a 1 m × ⅛ in. column of 20% SE-30 on Chromosorb A 60/80 Mesh: T$_c$ = 75°; Flux of N$_2$ 175 ml/min; retention time 330 s.

Bromoacetaldehyde. This product was obtained by the reaction of bromodioxonium bromide[19] with acetaldehyde as described by Yanovskaya *et al.*[6]

Starting with 22.0 g (0.5 mol) of acetaldehyde the following fractions were obtained by distillation: (i) b.p. 44–50°/70 torr, 20.67 g, 50% by weight (NMR) of bromoacetaldehyde and 1,4-dioxane. (ii) b.p. 50–67°/70 torr, 4.31 g, 68% by weight (NMR) of bromoacetaldehyde and 1,4-dioxane. The total yield was 13.3 g (0.108 mol; 26%) of bromoacetaldehyde dissolved in 1,4-dioxane. The product is unstable even at −15° and was employed immediately.

(E)-5-Bromo-3-penten-2-one (3; X = Br).

(i) *Via allylic bromination.* This reaction is described by Awang and Vincent.[3] In a 50 ml flask fitted with a reflux condenser and a calcium chloride tube were introduced 0.84 g (11 mmol) of (E)-3-penten-2-one, 1.95 g (11 mmol) of N-bromosuccinimide, 0.84 g (15 mmol) of calcium oxide,[5] 1.05 g (13 mmol) of sodium bicarbonate,[5] 13 ml of anhydrous benzene and 100 mg of benzoyl peroxide as catalyst. The mixture was irradiated for 22 min with a 500 W sunlamp. Filtration of the crude mixture gave a pale yellow solution containing (E)-5-bromo-3-penten-2-one and (E)-3-penten-2-one in the molar ratio 1:1 (NMR), which was used as such in the next step.

(ii) *Via Wittig condensation.* To a stirred solution of 34.4 g (0.108 mol) of **14** in CH$_2$Cl$_2$ (110 ml) was added dropwise a solution of 13.3 g (0.108 mol) of bromoacetaldehyde in 11.7 g of 1,4-dioxane and 25 ml of CH$_2$Cl$_2$. The resulting solution was stirred in the dark for two days at room temperature. Vacuum elimination of solvents and repeated washings of the oily residue with hexane (≃ 900 ml; the residue solidified upon washing) afforded a solution from which Ph$_3$PO separated after standing overnight at 4°. Filtration and concentration to 250 ml yielded a solution of the desired (E)-5-bromo-3-penten-2-one which was used in the next step.

4-Oxo-2-pentenyltriphenylphosphonium bromide, 5-Br and 4-oxo-1-pentenyltriphenylphosphonium bromide, 10-Br

(i) *Using* (E)-5-bromo-3-penten-2-one *obtained by allylic bromination.* A benzene solution of (E)-3-penten-2-one and (E)-

5-bromo-3-penten-2-one (starting from 11 mmol of pentenone) was added under inert atmosphere to a stirred solution of 2.0 g (8 mmol) of dry triphenylphosphine, 35 ml of anhydrous THF and three drops of triethylamine.[20] The mixture was stirred at room temperature for one hour and was left standing two more hours; after this time a red oil was formed.

The solvent was eliminated at reduced pressure and the remaining oil was crystallized (after several attempts) by adding a few drops of ethanol and anhydrous THF and storing the flask overnight at 4°. 1.396 g (3.3 mmol) of a 3:1 mixture of 5-Br and 10-Br (m.p. 171–185°) were obtained after filtration. The overall yield from the pentenone to the phosphonium salts was 32%. The analytical sample was recrystallized twice from absolute ethanol-anhydrous ether (m.p. 183–186°). The ^{1}H NMR spectrum was identical to the one described by Zbiral.[11] Elemental analysis for C$_{23}$H$_{22}$BrOP: Calc. C: 64.95; H: 5.21; Br: 18.79. Found C: 65.05; H: 5.21; Br: 18.95%.

(ii) *Using bromopentenone obtained by Wittig condensation.* An analogous procedure as described before was followed with the hexane solution. Starting with 13.3 g (0.108 mol) of bromoacetaldehyde, 6.33 g (14.9 mmol) of 5-Br and 10-Br (m.p. 178–185°) were obtained. The overall yield of both reactions was 14%.

Reaction of 5-Br and 10-Br with benzaldehyde

5.9 ml of a 0.85 N solution of potassium *ter*-butoxide in *ter*-butanol were added under inert atmosphere to a suspension of 2.16 g (5.1 mmol) of 5-Br and 10-Br in 50 ml of anhydrous benzene. After 30 min a solution of 0.56 g (5.3 mmol) of benzaldehyde in 10 ml of absolute benzene was added. The mixture was stirred at room temperature overnight and afterwards was filtered. The filtrate was washed, dried over Na$_2$SO$_4$ and the solvent was removed under vacuum obtaining a crude, which was extracted several times with ether. This extract (1.01 g) was distilled and the fraction with b.p. 130–160°/0.1 torr was collected (0.166 g; 19%). Preparative TLC with hexane–ether (4–1) afforded 53.4 mg of (3E,5E)-6-phenyl-3,5-hexadien-2-one[14] **7**, (m.p. 65–68°) and 22.2 mg of (Z)-3-benzylidene-4-penten-2-one, **8**, [δ = 2.45 (3H, s); 5.4 (2H, J$_{13}$ = 18 Hz), J$_{23}$ = 11 Hz, J$_{12}$ = 2 Hz); 6.5 (1H, J$_{31}$ = 18 Hz, J$_{32}$ = 11 Hz); 7.3 (1H, s); 7.47 (5H, s)].

Reaction of 5-Br and 10-Br with 4-nitrobenzaldehyde

As described for the condensation with benzaldehyde, a mixture of 2.20 g (5.2 mmol) of 5-Br and 10-Br, 6.0 ml of a 0.85 N solution of potassium *ter*-butoxide in *ter*-butanol and 0.783 g (5.2 mmol) of 4-nitrobenzaldehyde was allowed to react overnight at room temperature. The crude mixture was filtered and the filtrate was washed with water, dried over Na$_2$SO$_4$ and the solvent was removed under vacuum. The crude (2.62 g) was filtered through 26 g of SiO$_2$ with hexane-CH$_2$Cl$_2$ (1–1) obtaining 0.686 g (3.2 mmol; 61%) of (3E,5Z-E)-6-(4-nitrophenyl)-3,5-hexadien-2-one 12, Only the major isomer (3E,5E)-12[15] was obtained pure (m.p. 129–130°). ^{1}H NMR of (3E,5E)-12 (CDCl$_3$): δ = 2.35 (3H, s); 6.38 (1H. J = 15 Hz); 6.95–7.55 (3H, m); 7.60, 7.73, 8.22 and 8.35 (4H, AA'BB' system).

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