(Benzoyliodomethyl)triphenylphosphonium Iodide: A Convenient Reagent for Direct Synthesis of Arylethynyl Phenyl Ketones by Chain Extension of Aldehydes

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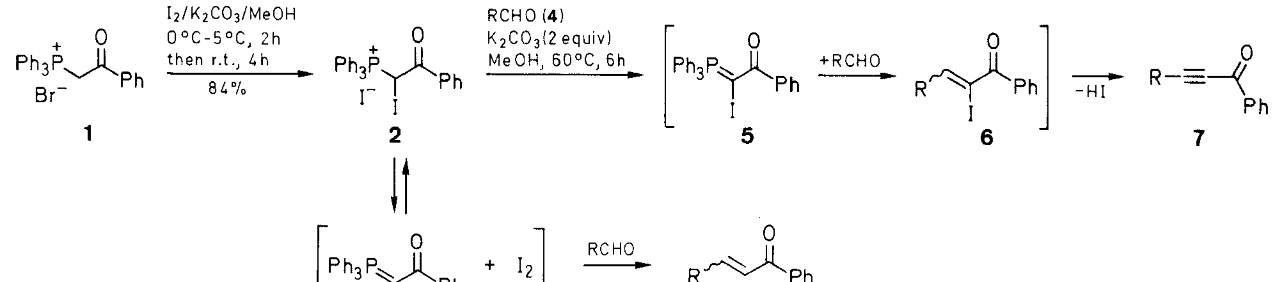
Reaction between (benzoyliodomethyl)triphenylphosphonium iodide, potassium carbonate and various aromatic aldehydes in a liquid–solid two-phase system, gives arylethynyl phenyl ketones in good yield.

The transformation of aldehydes to acetylene derivatives by chain extension is of considerable value in organic synthesis. All the formyl–alkynyl conversion methods which include Wittig reaction of (halo- or dihalomethylene) triphenylphosphorane yield initially, haloalkenes, which afford acetylenes by dehydrohalogenation.[1–3] Similarly pyrolysis of stable bisacyl phosphoranes yields acetylenic ketones.[4–7]. This last method presents some difficulties in large scale preparation and often results in a mixture of ketones. In a previous communication[8] the use of iodophosphorane in the synthesis of acetylenic esters and acids was described. We report here a novel, one-step synthesis of arylethynyl phenyl ketones using (benzoyliodomethyl)triphenylphosphonium iodide (**2**), obtained from (benzoylmethyl)triphenylphosphonium bromide (**1**) by direct iodination in methanol in presence of potassium carbonate.

(Benzoyliodomethyl)triphenylphosphonium iodide (**2**) reacts with aromatic or α,β-unsaturated aldehydes **4** in a



4, 6, 7	R	4, 6, 7	R	4, 6, 7	R	4, 6, 7	R
a	Ph	d	$2\text{-}O_2NC_6H_4$	g	$2,5\text{-}(MeO)_2C_6H_3$	i	$2,4\text{-}Cl_2C_6H_3$
b	$2\text{-}MeOC_6H_4$	e	$3\text{-}O_2NC_6H_4$	h	$2\text{-}ClC_6H_4$	j	Ph–CH=CH
c	$4\text{-}MeOC_6H_4$	f	$4\text{-}O_2NC_6H_4$				

Scheme

Table. Arylethynyl Phenyl Ketones 7a–j Prepared

Product	Yield[a] (%)	mp (°C)[b]	Molecular Formula[c] or Lit. mp (°C)	IR (KBr or melt)[d] ν(cm^{-1})	UV (EtOH)[e] λ_{max} (nm) (log ε)	^{1}H-NMR (CDCl$_3$/TMS)[f] δ
7a	64	48	48[10]	2200, 1650	258 (3.76)	6.40–7.80 (m)
7b	63	oil	$C_{16}H_{12}O_2$ (236.2)	2200, 1660	338 (3.70), 292 (3.76), 257 (3.76)	3.50 (s, 3H), 6.20–7.90 (m, 9H)
7c	60	81–82	81[10]	2195, 1710	336 (3.83), 265 (3.86)	3.90 (s, 3H), 6.90–8.20 (m, 9H)
7d	62	58	$C_{15}H_9NO_3$ (251.2)	2210, 1720	267 (3.74)	7.30–8.50 (m)
7e	58	60	$C_{15}H_9NO_3$ (251.2)	2200, 1710	265 (4.04)	7.25–8.55 (m)
7f	61	148	148–145[10]	2210, 1720	265 (4.08)	7.20–8.30 (m)
7g	66	oil	$C_{17}H_{14}O_3$ (266.2)	2195, 1710	259 (3.93), 294 (3.83)	3.7 (s, 3H), 3.8 (s, 3H), 6.8–8.1 (m, 8H)
7h	66	94	$C_{15}H_9ClO$ (240.6)	2210, 1715	288 (3.69)	6.90–7.90 (m)
7i	64	128	128–129[9]	2200, 1675	295 (3.80)	7.15–8.45 (m)
7j	65	68	$C_{17}H_{12}O$ (232.2)	2200, 1650, 1575	330 (4.23)	7.00–7.60 (m, 9H), 7.7–8.1 (m, 2H)

[a] Yield of isolated product after chromatography.
[b] Uncorrected and recorded with a Kofler apparatus.
[c] Satisfactory microanalyses obtained: C ±0.24, H ±0.16.
[d] Recorded on a Perkin-Elmer 297 spectrophotometer.
[e] Recorded on a Beckmann Acta M_4 spectrophotometer.
[f] Recorded on a R-24B Hitachi Perkin Elmer spectrometer.

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solid–liquid two-phase system to give arylethynyl phenyl ketones as the final product. Mechanistically, the initial step of the reaction is deprotonation of **2** to give (benzoyliodomethylene)triphenylphosphorane (**5**), which reacts with the aldehyde **4**. The intermediate from this reaction, the 2-iodo-2-alken-1-one **6** easily undergoes hydro-iodo-elimination with potassium carbonate to give arylethynyl phenyl ketones **7**. In every reaction a low yield of arylalkenyl phenyl ketone is obtained, probably as a result of the equilibria between **2** and **3**.[2] No condensation was obtained with aliphatic aldehydes.

The advantages of this procedure are reasonable yields, the short reaction time, and the ease with which the reaction can be performed in a one-step procedure with readily available starting materials.

All reagents were of commercial quality, (benzoylmethyl)triphenylphosphonium bromide was purchased from Aldrich Chemical Co.

(Benzoyliodomethyl)triphenylphosphonium Iodide (2):
A solution of I_2 (17.78 g, 0.070 mol) in MeOH (70 mL) is added dropwise at 0–5 °C to a well-stirred, two-phase system consisting of solid K_2CO_3 (9.66 g, 0.070 mol) and (benzoylmethyl)triphenylphosphonium bromide (32.36 g, 0.070 mol) in MeOH (70 mL). The temperature is maintained between 0–5 °C for 2 h and then at r.t. for 4 h. A lemon-yellow precipitate appears, is collected by filtration and washed with cold MeOH (20 mL). The crude product is stirred in H_2O (200 mL) until the H_2O remains neutral. The resultant solid is filtered, dried under vacuum in presence of P_2O_5, and stored at 0 °C in the dark; yield: 37.3 g (84 %); mp 204–205 °C.

$C_{26}H_{21}I_2OP$	calc.	C 49.35	H 3.33	I 40.06	P 4.88
(634.3)	found	49.38	3.33	38.2	4.89

IR (KBr): ν = 1650 cm^{-1} (C=O).

UV (EtOH): λ max = 289, 275, 259 nm.

^{1}H-NMR ($CDCl_3$/DMSO-d_6)/TMS): δ = 2.7 (d, 1 H, CH), 7.55–8.20 (m, 20 H_{arom}).

Synthesis of Arylethynyl Phenyl Ketones 7a–j; General procedure:
A solution of aldehyde **4** (0.02 mol) in MeOH (30 mL) is added dropwise to a suspension of (benzoyliodomethyl)triphenylphosphonium iodide (12.68 g, 0.02 mol) and K_2CO_3 (5.52 g, 0.04 mol) in MeOH (40 mL) at r.t. The mixture is heated for 6 h at 60 °C, then allowed to cool to r.t., filtered and evaporated under reduced pressure. To the residue, H_2O (100 mL) and Et_2O (100 mL) are added with stirring. The organic layer is separated and washed with 10 % HCl (20 mL) and evaporated to dryness. Products **7a–j** are purified and separated, from their corresponding alkenyl ketones by column chromatography on silica gel using toluene as the eluent.

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