A Facile Synthesis of Substituted 4-Acetylstilbenes

Ram S. Tewari*, Suresh C. Chaturvedi

Department of Chemistry, H. B. Technological Institute, Kanpur-208002, India

The literature[1] reveals that Friedel-Crafts acetylation of stilbene gives 4,4'-diacetylstilbene; in no case was a monoacetylated stilbene obtained. The synthesis of substituted monoacetylstilbenes could not be achieved by other conventional methods adopted for the preparation of stilbenes. Prompted by these reports and following our interest in the reactivity alkylidenearsoranes[2, 3, 4] we wish to report a convenient route for the synthesis of substituted 4-acetylstilbenes by two different routes using 4-acetylbenzylidenetriphenylphosphoranes and the corresponding arsoranes.

Our method consists of the reaction of 4-bromomethylacetophenone (**1**) with an equimolar amount of triphenylphosphine (**2a**) or triphenylarsine (**2b**) in boiling benzene, conversion of the resultant phosphonium (**3a**) or arsonium salt (**3b**) to the phosphorane (**4a**) or arsorane (**4b**) by treatment with base, and reaction of **4a, b** (which cannot be isolated because of their instability and sensitivity towards air and moisture) with benzaldehydes (**5**). The structure of the ethylene derivatives **6** thus obtained were established by microanalyses, physical, and spectral data.

The arsorane **4b** seems to be more reactive towards benzaldehydes than the phosphorane **4a** as can be seen from the better yields of **6** obtained using **4b**. This higher reactivity of **4b** may be attributed to the lower d_π-p_π resonance of **4b** as compared to **4a**.

When the intermediates **4a, b** are generated using sodium methoxide in methanol they do not undergo the reaction (cf. Ref. [5]). However, when two equivalents of 4-methylbenzaldehyde are added to the solution containing **4a** or **4b** and the mixture is stirred for 3–4 h, 4-methyl-4'-(4-methylcinnamoyl)-stilbene (**7**) is obtained as a thick yellow precipitate by simultaneous aldol condensation and carbonyl olefination.

4-Acetylbenzyltriphenylphosphonium Bromide (3a):
A solution of triphenylphosphine (**2a**; 5.24 g, 0.02 mol) in benzene (30 ml) is added dropwise, with stirring, to a solution of 4-bromomethylacetophenone (**1**; 4.26 g, 0.02 mol) in benzene (30 ml) under a nitrogen atmosphere. The resultant mixture is refluxed for 4 h and then allowed to stand overnight. The salt **3a** is collected by filtration, dried, and recrystallized twice from chloroform/hexane; yield: 7.4 g (78 %); colorless crystals, m.p. 247–249°.

$C_{27}H_{24}BrOP$	calc.	C 68.21	H 5.05
(475.4)	found	68.24	5.07

I.R. (KBr): $\nu_{max}=1725\,cm^{-1}$ (C=O).

^{1}H-N.M.R. (CDCl$_3$): $\delta=2.64$ (s, 3H, CO—CH$_3$); 5.75 (d, 2H, P—CH$_2$, $J_{PH}=15$ Hz); 7.30–8.20 ppm (m, 19 H$_{arom}$).

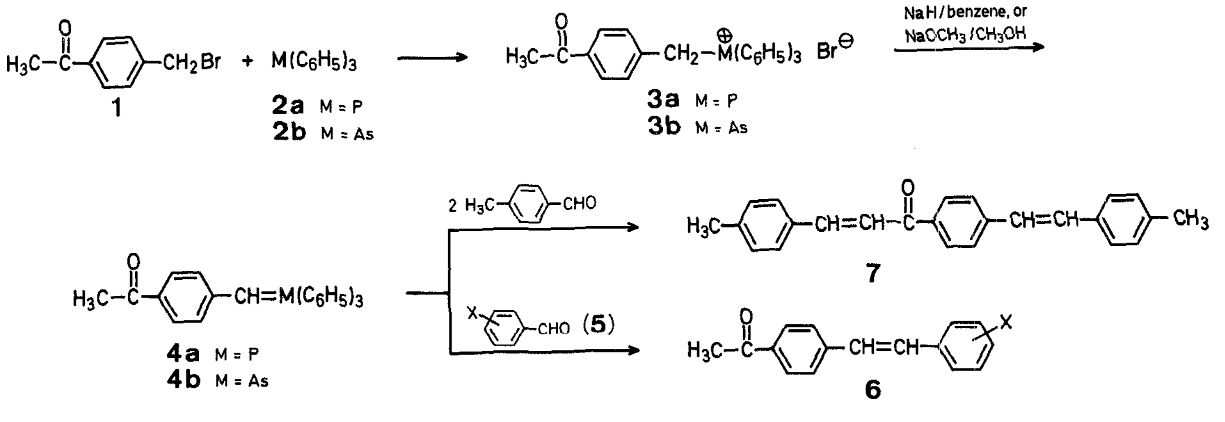
4-Acetylbenzyltriphenylarsonium Bromide (3b):
A solution of triphenylarsine (**2b**; 12.2 g, 0.04 mol) and 4-bromomethylacetophenone (**1**; 8.52 g, 0.04 mol) in benzene (60 ml) is refluxed for 3 days. Excess solvent is then evaporated on a steam bath and ethyl acetate (30 ml) is added to the residue (~ 15 ml). The precipitated salt **3b** is isolated by filtration and recrystallized twice from chloroform/benzene to give a microcrystalline product; yield: 12.6 g (60 %); m.p. 167–168°.

$C_{27}H_{24}AsBrO$	calc.	C 62.42	H 6.42
(519.3)	found	62.48	6.37

I.R. (KBr): $\nu_{max}=1725\,cm^{-1}$ (C=O).

^{1}H-N.M.R. (CDCl$_3$): $\delta=2.35$ (s, 3H, CO—CH$_3$); 6.30 (s, 2H, As—CH$_2$); 7.13–8.42 ppm (m, 19 H$_{arom}$).

Preparation of 4-Acetylstilbenes (6); General Procedure:
A suspension of phosphorane **4a** or arsorane **4b** is prepared by adding sodium hydride (96 mg, 4 mmol) to the phosphonium salt **3a** (1.9 g, 4 mmol) or arsonium salt **3b** (2.08 g, 4 mmol), respectively, in benzene (100 ml) under a nitrogen atmosphere. To this suspension, the benzaldehyde **5** (4 mmol) is added and the mixture is stirred for 6–8 h at room temperature. The solid product is filtered off and the filtrate is evaporated on a steam bath. The



0039-7881/78/0832-0616 $ 03.00

Table. 4-Acetylstilbenes (**6**) prepared

X	prep-ared from	Yield [%]	Recrystal-lization solvent	m.p.[a]	Molecular formula[b]	I.R. (KBr) ν_{max} [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$) δ [ppm]
H	**3a**	42	benzene/hexane	160–161°	$C_{16}H_{14}O$	1661[c]; 1600[d];	
	3b	56	benzene/hexane	158–159°	(222.3)	938[e]	
4-NO_2	**3a**	70	*benzene/hexane*	*187–189°*	$C_{16}H_{13}NO_3$	*1681*[c]; *1613*[d];	2.63 (s, 3H, CO—CH_3); 7.16–7.36 (q, 2H_{olefin}); 7.53–8.33 (m, 8H_{arom})
	3b	85	benzene/hexane	188–190°	(267.3)	960[e]	
4-$N(CH_3)_2$	**3a**	58	benzene/PE	228–230°	$C_{18}H_{19}NO$	1676[c]; 1608[d];	2.60 (s, 3H, CO—CH_3); 3.05 [s, 6H, $N(CH_3)_2$]; 6.75–7.20 (q, 2H_{olefin}); 7.32–8.15 (m, 8H_{arom})
	3b	70	benzene/PE	231–233°	(265.3)	950[e]	
3,4-O—CH_2—O—	**3a**	54	benzene/hexane	*153–154°*	$C_{17}H_{14}O_3$	*1672*[c]; *1605*[d];	*2.60 (s, 3H, CO—CH_3);* 6.02 (s, 2H, O—CH_2—O); 6.85–7.28 (q, 2H_{olefin}); 7.38–8.20 (m, 7H_{arom})
	3b	76	benzene/hexane	154–156°	(266.3)	955[e]	

[a] Melting points were determined using a Gallenkamp apparatus and are uncorrected.

[b] The microanalyses were in good accord with the calculated values: C, ±0.07; H, ±0.07.

[c] C=O.

[d] C=C.

[e] Out-of-plane deformations of the H-atom of the *trans*-olefinic system.

residue is chromatographed over neutral alumina using benzene/petroleum ether (40–60°) (1:1) as eluent. The product is recrystallized from the solvent given in the Table.

4-Methyl-4'-(4-methylcinnamoyl)-stilbene (7):

A solution of phosphorane **4a** or arsorane **4b** is prepared by adding sodium methoxide (4 mmol) to a solution of the phosphonium salt **3a** (0.95 g, 2 mmol) or arsonium salt **3b** (1.04 g, *2 mmol), respectively, in methanol (50 ml) under a nitrogen atmosphere*. To this solution, 4-methylbenzaldehyde (0.48 g, 4 mmol) is added and the mixture is stirred for 2 h at room temperature. The resultant yellow solid is isolated by filtration, washed with water, dried, and recrystallized from chloroform/hexane (1:1); yield from **3a:** 0.34 g (50%); m.p. 221–223°; yield from **3b:** 0.40 g (60%); m.p. 218–220°.

$C_{25}H_{22}O$	calc.	C 88.75	H 6.50
(338.4)	found	88.69	6.43

M.S.: *m/e* = 338 (M^+, 12%), 337 (75), 336 (100), 323 (85), 308 (25), *221 (54), 177 (58), 161 (66), 145 (54), 117 (40), 105 (20)*, 91 (27).

I.R. (KBr): ν_{max} = 1667 cm^{-1} (C=O).

U.V. (CHCl$_3$): λ_{max} = 356 nm.

^{1}H-N.M.R. (CDCl$_3$): δ = 2.05 (s, 6H, 2CH$_3$); 6.66–7.15 (m, 4H_{olefin}); 7.20–7.71 ppm (m, 12H_{arom}).

The authors thank Dr. S. D. Shukla, H.B.T.I., Kanpur-2, India, for providing facilities. S.C.C. thanks CSIR, New Delhi (India) for the award of Senior Research Fellowship.

Received: October 4, 1977
(Revised form: December 19, 1977)

---

* Author to whom correspondence should be addressed.

[1] W. C. J. Ross, *J. Chem. Soc.* **1945**, 536.

[2] P. S. Kendurkar, R. S. Tewari, *J. Organomet. Chem.* **60**, 247 (1973); **85**, 173 (1975).

[3] R. S. Tewari, K. C. Gupta, S. C. Chaturvedi, *Z. Naturforsch.* [b] **32**, 1165 (1977).

[4] R. S. Tewari, S. C. Chaturvedi, *Tetrahedron Lett.* **1977**, 3843.

[5] J. A. Elix, *J. Chem. Soc. Chem. Commun.* **1968**, 343.

0039-7881/78/0832-0617 $ 03.00