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FACILE FORMYLOLEFINATION OF ALDEHYDES BY MEANS OF ARSONIUM SALT[1]

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Abstract: A facile formylolefination of a variety of aldehydes was achieved by using formylmethyltriphenylarsonium bromide with K_2CO_3 (trace H_2O) at room temperature to give highly stereoselectively (E) α,β-unsaturated aldehydes in excellent yields.

Reactions which convert carbonyl compounds to α,β-unsaturated aldehydes are highly useful synthetic operation, especially for the synthesis of biologically active natural products. When formylmethylenetriphenylphosphorane was used, the reaction should be carried out under rather drastic conditions.[2,3] Alternatively, the formyl-group masked Wittig reagent or phosphoryl reagent was used, the products should be subjected to acid hydrolysis which may be incompatible with complex synthesis.[4,5] Another method for formylolefination was treating the carbonyl compounds with cis-2-ethoxyvinyllithium which suffered from the difficulty to prepare.[6] In continuation of our studies on arsonium ylides,[7,8] we now wish to report a facile formylolefination of a variety of aldehydes by using formylmethyltriphenylarsonium bromide directly with K_2CO_3 (trace H_2O) at room temperature to give highly stereoselectively (E) α,β-unsaturated aldehydes in excellent yields. The results are shown in the Table.

$$\underset{\underline{1}}{(C_6H_6)_3\overset{+}{As}\text{-}CH_2CHO\ Br^-} + \underset{\underline{2}}{RCHO} \xrightarrow[THF\text{-}Et_2O,\ r.t.\ -Ph_3AsO]{K_2CO_3(s),\ \text{trace}\ H_2O} \underset{\underline{3}}{RCH{=}CHCHO}$$

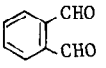
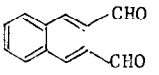
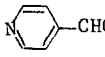
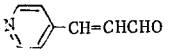
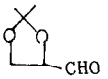
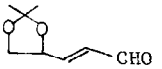
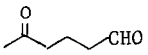
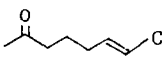
The reagent 1 was easily prepared from triphenylarsine and bromoacetaldehyde (in dioxane)[9] in acetonitrile at room temperature for 9 hrs in 90% yield.[10] (E) α,β-unsaturated aldehydes were synthesized stereoselectively and chemoselectively(Entry 9)[11] under mild conditions. The products of Entry 7 and 8 could be served as the useful intermediates for the synthesis of sex pheromone of Prionoxystus robiniae[12] and 11(R)-HETE,[13] lipoxygenation product of arachidonic acid, respectively. The yields reached 81-98% in all cases. Furthermore,the by-product triphenylarsine oxide could be easily removed from the desired product by passing through a small amount of silica gel, and reconverted to triphenylarsine by reduction.[14]

Typical Procedure:

Reagent 1 (2.4 mmol), $n\text{-}C_8H_{17}CHO$ (2 mmol), $THF\text{-}Et_2O$(3:7) 20ml, trace H_2O were mixed in a reaction tube under N_2 and stirred at room temperature. After the reaction was complete (monitored by GC or TLC), the solvent was evaporated under reduced pressure. The residue was extracted with ether and the solution was passed through a small amount of silica gel to remove

most of triphenylarsine oxide. The desired crude α,β-unsaturaed aldehyde was purified by flash chromatography.

Table Formylolefination of aldehydes

Entry	Substrate	Reaction Time (hrs)	Product[a] (E isomer>97%)	Yield (%)
1	p-O_2N-C_6H_4CHO	4	p-O_2N-C_6H_4CH=CHCHO	96
2	p-ClC$_6H_4$CHO	20	p-ClC$_6H_4$CH=CHCHO	93
3	C_6H_5CHO	20	C_6H_5CH=CHCHO	87
4		16		86[b]
5		9		98
6	n-C_5H_{11}CHO	17	n-C_5H_{11}CH=CHCHO	81
7	n-C_8H_{17}CHO	24	n-C_8H_{17}CH=CHCHO	89
8		3		91
9		13		85

a) All the products were confirmed by ^1H NMR, IR and MS. E isomers were determined by GC and ^1H NMR. b)  : 1 = 1:2.4 (mole ratio).

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References and Notes:

1. This paper is the 40th report on the studies of the application of elemento-organic compounds of fifth and sixth groups in organic syntheses.
2. S. Trippett, D.M. Walker, J.Chem.Soc., 1266 (1961).
3. H.J. Bestmann, O. Vostrowsky, H. Paulus, W. Billmann, W. Stransky, Tetrahedron Lett., 121 (1977).
4. T.M. Cresp, M.V. Sargent, P.Vogel, J.Chem.Soc. Perkin I, 37 (1974).
5. Wataru Nagata, Yoshio Hayase, Tetrahedron Lett., 4359 (1968).
6. R.H.Wollenberg, K.F. Albizati, R. Peries, J.Am.Chem.Soc., 99 7365 (1977).
7. Y.Z. Huang, Y.C. Shen, Adv. Organomet. Chem., 20, 115 (1982).
8. Shi Lilan, Xiao Wenjuan, Ge Yuting, Huang Yaozeng, Acta Chim . Sinica, in press.
9. L.A. Yanovskaya, A.P. Terrent'ev, L.I. Belen'kii, J.Gen.Chem. U.S.S.R., 22 1594 (1952).
10. The reagent 1 gave satisfactory elemental analysis (± 0.3%) m.p. 160-161°C; ^1H NMR (60 MHz, $CDCl_3$); 9.99(s, 1H), 7.63(m, 15H), 5.91(s, 2H),; IR: 2840, 2880, 1705 cm^{-1}(CHO);
11. The product of Entry 9 gave satisfactory elemental analysis (±0.3%); ^1H NMR(60 MHz,CCl_4, δ): 9.37(d, J=7.8 Hz, 1H), 6.68(dt, J=16, 7.0 Hz, 1H), 5.96(dd, J=16, 7.8 Hz, 1H), 2.36 (m, 4H), 2.07(s, 3H), 1.66 (m, 2H); IR: (film): 1692 cm^{-1} (CHO), 1715 cm^{-1}(CH_3CO), 980 cm^{-1} (trans CH=CH); MS: 141 (M+1), 83, 58,43.
12. C.A. Henrick, Tetrahedron 33, 1845 (1977).
13. E.J. Corey, J. Kang, J.Am.Chem.Soc., 103, 4618 (1981).
14. Yi De Xing, Xue Long Hou, Nai Zheng Huang, Tetrahedron Lett., 22, 4727 (1981); Lu Xi-Yan, Wang Qi-Wen, Tao Xiao-Chun, Sun Jun-Hui, Lei Gui-Xin, Acta. Chim. Sinica, 43, 450 (1985).

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