BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (1), 367 (1975)

Synthesis of *o*-Ethynylcinnamaldehyde

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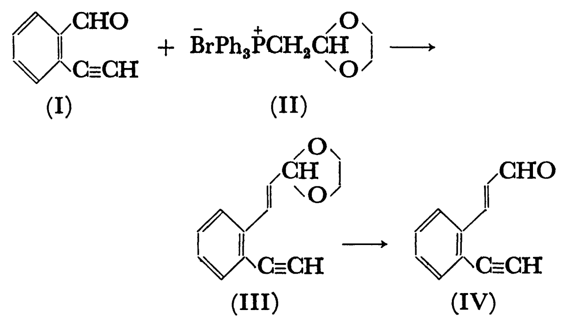
(Received July 1, 1974)

Synopsis. A synthesis of *o*-ethynylcinnamaldehyde(IV) starting from *o*-ethynylbenzaldehyde(I) by the Wittig reaction is described.

In a previous paper, we reported a synthesis of *o*-ethynylbenzaldehyde(I) and an attempt to synthesize dibenzo[18]annulene.[1] As an extension of our work on benz-fused annulenes, we found it necessary to synthesize *o*-ethynylcinnamaldehyde(IV). Howes *et al.* recently described syntheses and properties of [13],[15], [17]-membered annulenones and heteroannulenes.[2] For realizing the effect of annelation of benzene nuclei on the conjugated systems, the title compound is considered to be a key intermediate for syntheses of these benz-fused compounds.



The synthesis of *o*-ethynylcinnamaldehyde(IV) was carried out as follows.

The method of Müller-Cunradi and Pieroh[3] has been used extensively in the synthesis of $\alpha\beta$-unsaturated aldehyde. We used this method to prepare the title compound, the starting *o*-ethynylbenzaldehyde being recovered. Cresp, Sargent, and Vogel[4] have reported the use of 1,3-dioxolan-2-yl-methyltriphenylphosphonium bromide(II) in the syntheses of some $\alpha\beta$-unsaturated aldehydes. We applied their method to *o*-ethnylbenzaldehyde(I). The desired *o*-ethynylcinnamaldehyde(IV) was obtained with a satisfactory yield.

Experimental

The melting point is uncorrected. The electronic spectrum and infrared spectrum were taken on Hitachi-124 and Hitachi-EPI-S2 spectrophotometers, respectively, and the NMR spectrum and mass spectrum on JEOL-JNM-MH-60 and JEOL-JMS′-OI-SG′-2 spectrometers, respectively.

o-Ethynylcinnamaldehyde(IV): Lithium methoxide prepared from lithium (327 mg, 0.047 gatm) in dry methanol (150 ml) was added dropwise with stirring under nitrogen at 80—90 °C for 3 hr to *o*-ethynylbenzaldehyde(I) (4.0 g, 0.031 mol) and 1,3-dioxolan-2-yl-methyltriphenylphosphonium bromide (II) (20 g, 0.047 mol) in dry *N*,*N*-dimethylformamide (150 ml). After addition of the base, the reaction mixture was stirred under nitrogen at 82—85 °C for further 5 hr.

The reaction mixture was then poured into water (1800 ml) and extracted thoroughly with ether. The ether extract was washed with saturated brine, dried over sodium sulfate and evaporated.

The residue thus obtained was stirred at room temperature with tetrahydrofuran (150 ml) and 10% aqueous hydrochloric acid (150 ml) for 3 hr. After addition of water (150 ml), the reaction mixture was extracted with ether and the extract was washed with water, saturated aqueous sodium bicarbonate and water successively. After being evaporated, the residue was chromatographed on alumina (200 g) and the column was eluted with a mixture of light petroleum ether–ether (9: 1). Solids obtained after evaporating were collected (3.12 g, 67%) and recrystallized from *n*-hexane affording yellow needles. Mp, 89—90 °C. Found: C, 84.33; H, 4.95%; mol wt (mass spectroscopy) 156 (M^+, 65%), 128 (base). Calcd for $C_{11}H_8O$: C, 84.59; H, 5.16%; mol wt 156.17: IR (KBr disc); 3250(s), 2060(w), 1685(s), 1620(m), 960(s): UV (in EtOH); $\lambda_{\max}$ (ε), 242 (24100), 247 (23100), 292 nm (21700): NMR (τ in $CDCl_3$) 0.14 (d, 1H, -CHO, J=8 Hz), 1.90 (d, 1H, vinyl H, J=16 Hz), 2.16—2.66 (m, 4H, aromatic), 3.20 (dd, 1H, vinyl H, J=8, 16 Hz), 6.53 (s, 1H, -C≡CH).

The authors are grateful to Prof. F. Sondheimer, University College London, for kindly providing unpublished results.

This research was financially supported by the grants from the Ministry of Education.

References

1) J. Ojima, T. Yokomachi, and T. Yokoyama, *Chem. Lett.*, **1972**, 633.

2) P. D. Howes, E. LeGoff, and F. Sondheimer, *Tetrahedron Lett.*, **1972**, 3691, 3695; P. J. Beeby and F. Sondheimer, *Angew. Chem. Intern. Ed. Engl.*, **11**, 833 (1972).

3) M. Müller-Cunradi and K. Pieroh, U.S.P. 2165962 (*Chem. Abstr.*, **33**, 8210 (1939); M. Iyoda, H. Miyazaki, and M. Nakagawa, *Chem. Commun.*, **1972**, 431.

4) T. M. Cresp, M. V. Sargent, and P. Vogel, *J. Chem. Soc. Perkin I*, **1974**, 37.