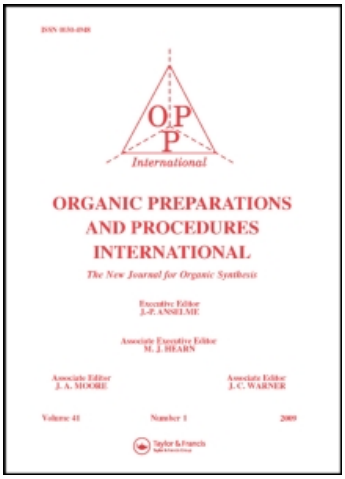

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THE PREPARATION OF (E)-2-PENTENAL

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The need for a large-scale preparative procedure for (E)-2-pentenal, a synthon for certain insect pheromones, has resulted in an improvement of Corey and Terashima's procedure[1] for the preparation of (E)-2-alkenals. The recycle of a tetrahydropyranyl (THP) ether of a propargylic alcohol (such as I in the Scheme) as well as two-step hydrolysis/isomerization of the allenic THP ether (II) to the (E)-enal (III) are now unnecessary.

$$\underset{\text{I}}{\text{Et-C}\equiv\text{C-CH}_2\text{-OTHP}} \xrightarrow[\text{2. HOAc}]{\text{1. n-BuLi}} \underset{\text{II}}{\text{Et-CH=C=CH-OTHP}} \xrightarrow[\text{H}^+]{\text{H}_2\text{O}}$$

$$[\text{Et-CH=C=CHOH}] \longrightarrow \underset{\text{III}}{(\text{E})\text{-Et-CH=CH-CHO}}$$

The improvements were effected by adding 5-10% of hexamethylphosphoric triamide (HEMPA) to the reaction solvent (THF). The allene: acetylene ratio reported[1] (2.3:1) rose to 8-16:1. Because the amount of I remaining was so small, recycle was unnecessary, and aqueous hydrolysis of II to III could be carried out directly using p-toluenesulfonic acid (p-TsOH) as catalyst. The two-phase system (H_2O:p-TsOH/CH_2Cl_2:allene-acetylene mixture) which we developed was refluxed until the THP ethers had been hydrolyzed [gas liquid chromatography (GLC) monitoring]. After removing the p-TsOH with aq. base, drying, and direct distillation,

yields of pure (E)-2-pentenal were 40% based on I.

EXPERIMENTAL

IR spectra of 5% solutions in 0.1 mm sealed NaCl cells were recorded on Perkin-Elmer 137 (CCl_4) or 457A (CS_2) spectrophotometers. NMR spectra were taken of 15% solutions (CCl_4, 2% TMS) in a Varian T-60. Ratios of allene-acetylene mixtures were determined by NMR or on a 4.7 m x 0.32 cm stainless steel (s.s.) column of Analabs (SD) base-washed (60-80 mesh) support with 5% diethylene glycol succinate (DEGS) substrate. The mixture of the aldehydes was analysed on a 4.7 m x 0.32 cm s.s. column of acid-washed Chromosorb W (60-80 mesh) supporting 15% HI-EFF-2AP (ethylene glycol adipate). Conditions for the DEGS column were: inj. port 170°; detector and col. 160°; air 240 mL/min; H_2 & N_2 30 mL/min; t_R = 6.5 min for $EtC{\equiv}CCH_2OTHP$ and t_R = 4.2 min for EtCH=C=CH-OTHP. Conditions for the HI-EFF column were: inj. & detector 150°; column 95°; air 240 mL/min; H_2 30 mL/min; N_2 15 mL/min; t_R [(Z)-2-pentenal] - 6.5 min; and t_R [(E)-2-pentenal] = 7.5 min. Sample injection size: 1.0 µL of 1% conc. in hexene or ether. Solv. were dried by distillation from, and stored over, CaH_2 (HEMPA) or distilled from $LiAlH_4$ and stored over CaH_2 (THF).

Tetrahydro-2-(2-pentynyloxy)-2H-pyran (I).- This was based on the procedure of Schwarz and Waters.[2] A 2.0 L round bottom flask with gastight mechanical stirrer, low-temp. thermometer, N_2 purge, pressure-equalized addition funnel and dry ice cooling bath, was charged with 56 g (1.0 mol) propargyl alcohol and 0.1 g p-TsOH. The flask was cooled in ice and 92.5 g (1.1 mol) 2,3-dihydropyran was added at 40° or below with stirring. The cooling bath was then removed and the mixture stirred 30 min, checked for -OH (IR), diluted with 700 mL THF, cooled to -30° to -70°, and treated during 30 min with 78.3 g (1.1 mol) n-BuLi (90% in hexane, Ventron) from a 100 mL valve-equipped syringe. The resultant lithium acetylide solution was warmed to 0° and treated at 10-30° with 135 g (1.2 mol) EtBr in 250 mL HEMPA/100 mL THF. The mixture was stirred 1.0 hr at room temperature and the volatiles then removed at 20 Torr/30-40° (water pump and bath). The residue was diluted with 2-3 vol. of light petroleum (b.p. 60-80°), washed with water and brine, and dried with $MgSO_4$. The tetrahydro-2-(2-pentynyloxy)-2H-pyran (I) was collected by distillation at 92°/8-10 Torr (96% yield). The IR and NMR data were consistent with

the assigned structure and with those of a sample prepared from dihydropyran and commercial 2-pentyn-1-ol.

(E)-2-Pentenal.-

Equipment.- A 3.0 L round bottom, 4-neck reaction flask with gastight mechanical stirrer, N_2 purge, low-temp. thermometer, and septums for adding reagents was connected (via a septum) by a dump tube to a 5.0 L round bottom quench flask also equipped with a mechanical stirrer, low-temp. thermometer, and N_2 purge. The dump tube was an 8 mm tube with a 4 mm stopcock. A 12/5 ball joint in the dump tube allowed for ease of assembly.

The reaction vessel was charged under N_2 with 1.0 L 1:19 v/v HEMPA/THF and 168 g (1.0 mol) I and chilled with stirring to -78°. The quench flask was charged with 2.5 L MeOH containing 66.0 g (1.1 mol) acetic acid and similarly chilled. From a valve-equipped syringe (100 mL) was added 74.7 g (1.05 mol) of n-BuLi (90% in hexane, Ventron). Addition required 20-30 min; the dark red reaction mixture was stirred for another 15-30 min and rapidly pushed through the dump tube (N_2 press.) into the very vigorously stirred quench solution. The solvents were removed (16-20 Torr, rotary evap.) and the residue (150+ g) was dissolved in 2-5 vol. H_2O, extracted with 3 portions of pentane, and dried with $MgSO_4$. The salt-free allenic-acetylenic THP ether mixture obtained after removal of the pentane (rotary evap.) could be used as such in the hydrolysis step. The allene:acetylene ratio (GLC) of 10-16:1 (usually 10:1) was corroborated by NMR-loss of -C-CH_2-O-: [δ 4.0 (2 H, m, J = 1.0 Hz, poorly resolved)].

A solution of the allene/acetylene THP ethers (1.0 g/3.0 mL CH_2Cl_2) was treated with 0.02 molar equiv. of p-TsOH and 1.2-1.4 molar equiv. H_2O. The mixture was heated to reflux for 3 hrs at 40° or until

complete hydrolysis of the THP ethers (GLC monitoring). The organic layer was then freed from the acid catalyst with $NaHCO_3$, dried with $MgSO_4$, and distilled, giving (E)-2-pentenal, bp. 117°/740 mm, lit.[3] bp. 62-64°/ 50 mm, directly in 40% yield.

Pure (E)-2-pentenal had: IR 1680 (O:C-C=C), 1625 (-CH=CH-), and 965 ($-CH^{t}{=}CH-$) cm^{-1}; the E/Z- mixture[1] (CCl_4) showed only minor differences; NMR of E/Z- mixture δ 9.95 [1 H, d, J = 7.5 Hz, Z- O=CH-], 9.33 [1 H, d, J = 7.0 Hz, E- O=CH-], and 6.2 [2 H, m, very poorly resolved, $-CH^{c}{=}{-}{=}CH^{t}-$]; the pure E-isomer had δ 1.3 [3 H, t, J = 6.0 Hz, CH_3-CH_2- CH=], 2.5 [2 H, q, J = 6.0 Hz, $CH_3-CH_2-CH=$], 5.9 [1 H, dd, J = 15 and 7.0 Hz, -CH=CH-CHO], 6.7 [1 H, dt, J = 15 and 6.0 Hz, $-CH_2CH=CH-CHO$], and 9.33 [1 H, d, J = 7.0 Hz, E- O=CH-].

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††† Mention of a commercial or proprietary product in this paper does not constitute an endorsement of this product by the U.S. Department of Agriculture.

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