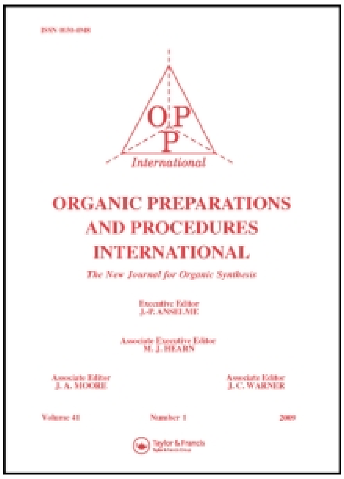

Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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To cite this Article Waters, R. M. , Voaden, D. J. and Warthen Jr., J. D.(1978) 'A PREPARATION OF (*Z,E*)-8,10-TRIDECADIEN-1-OL ACETATE', Organic Preparations and Procedures International, 10: 1, 5 — 8
To link to this Article: DOI: 10.1080/00304947809354996
URL: http://dx.doi.org/10.1080/00304947809354996

ORGANIC PREPARATIONS AND PROCEDURES INT. 10(1), 5-8 (1978)

A PREPARATION OF (Z,E)-8,10-TRIDECADIEN-1-OL ACETATE

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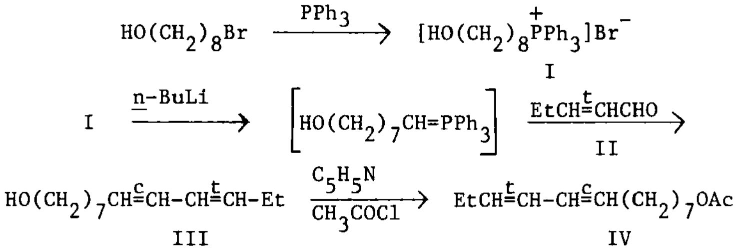
(Z,E)-8,10-Tridecadien-1-ol acetate (IV) was required for field testing as a synergist of (Z,E)-9,11-tetradecadien-1-ol acetate, the major component of the sex pheromone of Spodoptera littoralis (Boisduval),[1] the Egyptian cotton leafworm, and its Japanese counterpart S. litura (F.).[2]

Our synthetic approach to the desired (Z,E)-8,10-conjugation was



$$HO(CH_2)_8Br \xrightarrow{PPh_3} \underset{I}{[HO(CH_2)_8\overset{+}{P}Ph_3]Br^-}$$

$$I \xrightarrow{\underline{n}\text{-}BuLi} \left[HO(CH_2)_7CH{=}PPh_3\right] \xrightarrow[II]{EtCH\overset{t}{=}CHCHO}$$

$$\underset{III}{HO(CH_2)_7CH\overset{c}{=}CH\text{-}CH\overset{t}{=}CH\text{-}Et} \xrightarrow[CH_3COCl]{C_5H_5N} \underset{IV}{EtCH\overset{t}{=}CH\text{-}CH\overset{c}{=}CH(CH_2)_7OAc}$$

based on the Wittig condensation between (E)-2-pentenal (II)[3] and the phosphonium salt (I) derived from 8-bromo-1-octanol. Sonnet[4] showed that a high Z-alkene content (94-96%) could be obtained in hexamethylphosphoric triamide (HEMPA) and tetrahydrofuran (THF) at 10-15° using saturated aldehydes. It was hoped, therefore, that pure HEMPA at 0-5° might prevent isomerization of the conjugated ethylenic group of II as well as giving Z-coupling.

Our product typically contained, by GLC analyses, 5-6% of (E,E)-8,10-isomer (E-coupled) and 1-2% of (Z,Z)-8,10-isomer (Z-coupled, possible Z-impurity from the pentenal).[5] The range of E-coupling was 4-10%, agreeing with results reported by Sonnet. The double bond in the pentenal, which became conjugated in the reaction product, thus had not influenced the course of the reaction. The Z-configuration of the Δ^{10} position of the Z,Z-by-product may arise from some (Z)-2-pentenal impurity. GLC analysis of our pentenal did not detect the Z-isomer, though small amounts could have been present. GLC comparison of our materials with samples of (Z,E)-9,11-tetradecadien-1-ol acetate, thought to contain the C-13 diene acetate, indicated that the major impurity preceding the C-14 diene acetate was not this C-13 diene acetate.

EXPERIMENTAL

Mps. were determined on a MEL-TEMP apparatus and are uncorrected. Infrared spectra were measured with Perkin-Elmer 137 and 457A spectrophotometers. NMR spectra were recorded on a Varian T-60 as CCl_4 solutions with 2% TMS as the internal standard. GLC analyses were performed on a Varian 600-D with a 1.88 m x 0.32 cm stainless steel column of 5% Carbowax 20M-TPA on base-washed Chromosorb G (60/80 mesh) and on a Varian 204-1B with a 15.24 m x 0.55 mm DEGS SCOT column (Perkin-Elmer). Conditions for the Carbowax 20M-TPA column were: injection port 260°; detector and column 105°; N_2 and H_2 30 mL/min; air 240 mL/min. Injection samples ranged from 0.1 to 1.0 μL of a 1.0% solution in isooctane. Conditions for the DEGS SCOT column were: injection port 185°; detector 210°; column 135°; 3.8 mL He/min; make-up 24.8 mL He/min; 28.5 mL H_2/min; 300 mL air/min; injection split ratio 1:8. Sample size was 1.0 μL of a 1.0% solution in hexane. Thin layer chromatography (TLC) was carried out on 250 μm silica gel plates. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

(8-Hydroxyoctyl)triphenylphosphonium Bromide (I).- A solution of 0.1 mole of 8-bromo-1-octanol[6a] (bp. 80-85°/0.1 mm, lit.[6b] bp. 78-79°/0.1 mm) and 0.133 mole of PPh_3 in CH_3CN (150 mL) was refluxed 12-24 hr; the solvent was removed with a rotary evaporator (90°, 15 Torr). The syrupy salt was stirred vigorously at 100-110° with an equal volume of toluene. The mixture was allowed to cool slightly and the toluene decanted. This was repeated, if necessary, until the salt crystallized. The phosphonium bromide (yield 95-96%) was filtered, rinsed with hexane, and dried under continuous vacuum; mp 110° (shrank from 90°).

Anal. Calcd. for $C_{26}H_{32}BrOP$: Br, 16.95; P, 6.57.

Found: Br, 16.95; P, 6.60.

TLC of the salt (5% in CH_3CN; 9:1 $CH_3CN:H_2O$ as developer) showed one spot, R_f 0.55. Comparison on one plate with Ph_3PO, Ph_3P, and $HO(CH_2)_8Br$ gave R_fs 0.53, 0.63, 0.90, and 0.83 resp. IR(Nujol mull): 3350 (OH); 2325 (P-aryl stretch); and 1440 with 1110 (P-Ph) cm^{-1}.

(Z,E)-8,10-Tridecadien-1-ol Acetate (IV).- A 250 mL 4-neck round bottom flask with magnetic stirrer, thermometer, addition septums, and cooling bath was purged with N_2 and charged with 10.0 g (21.2 mmole) of I in 100 mL of distilled HEMPA (CaH_2-dried, added by syringe). After solution at 40-50°, the mixture was stirred at 0-5°, and 1.7 g (24 mmole, 10% excess) of 90% n-BuLi in hexane (Ventron) was added during 10 min. The temp. was 5-7° during addition and for 10 min thereafter. To the dark red soln. was added 2.0 g (25 mmole, 20% excess) of II during 10 min at 5°. The mixture was held at 5-10° for 0.5 hr, warmed to room temp. (0.5 hr), and treated with 16.7 g (0.21 mole, 10:1 molar ratio) of dry (CaH_2) pyridine. Acetyl chloride (6.6 g; 85 mmole, 4:1 molar ratio) was then added at or below 30°. The solution became light yellow; the temp. was then held at 50° 1 hr. The reaction mixture was cooled, poured into 1.0 L of ice/water and extracted with pentane. The extract was washed with 5% HCl, 5% $NaHCO_3$, satd. aq. NaCl solution, 4 x 5 mL of 9:1 DMSO:water, satd. aq. NaCl soln., dried over $MgSO_4$, and evaporated to give 4.4 g of material. Short-path distillation gave 3.0 g (60%) of C-13 diene acetate, bp. 104°/0.1 mm; IR 1743 s (-OAc), 1240 s (C-O), and 950 with 985 m ($CH\overset{c}{=}CH-CH\overset{t}{=}CH$) cm^{-1}. The ratio of the latter two spectral peaks (1:1.11) compared favorably with that (1:1.1-1.2) reported by Scholfield[7] for the diene system of pure methyl (Z,E)-9,11-octadecadienoates. GLC on the DEGS SCOT column revealed two very minor components closely trailing the major peak (t_R = 15 min); they were undoubtedly the Z,Z- and E,E-isomers.[5]

NMR: δ 1.00 (3 H, t, J = 7.0 Hz, $\underline{CH_3}-CH_2-CH=$), 1.3 (8-10 H, br. s,

$-(\underline{H}_2)_n-$), 1.95 (3 H, s, $C\underline{H}_3COO-$), 3.95 (2 H, t, J = 5.0 Hz, poorly resolved, $-C\underline{H}_2-OAc$), and 5.6 (4 H, m, very poorly resolved, $-CH\overset{c}{=}CH-CH\overset{t}{=}CH-$)

Anal. Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99.

Found: C, 75.81; H, 11.17.

Reduction of IV over Adams' catalyst gave *n*-tridecanol acetate, identical with an authentic sample by IR, vpc and tlc.

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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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(Received August 10, 1977; in revised form October 26, 1977)