Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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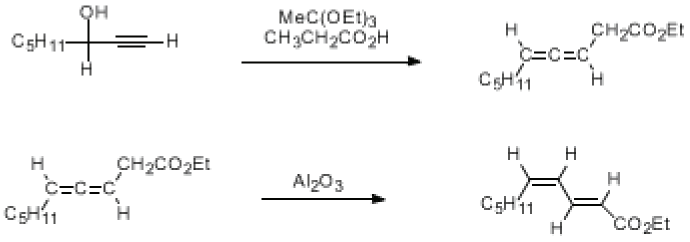
Organic Syntheses, Coll. Vol. 8, p.251 (1993); Vol. 66, p.22 (1988).

ETHYL (*E,Z*)-2,4-DECADIENOATE

[2,4-Decadienoic acid, ethyl ester, (*E,Z*)-]



Submitted by S. Tsuboi, T. Masuda, S. Mimura, and A. Takeda[1].
Checked by Mark A. Henderson and Clayton H. Heathcock.

1. Procedure

Caution! See benzene warning, Org. Synth., Coll. Vol. VI ***1988****, 68.*

A. *Ethyl 3,4-decadienoate* ***(1)***.[2] A 300-mL, round-bottomed flask equipped with a reflux condenser is charged with 12.1 g (0.096 mol) of 1-octyn-3-ol (Note 1), 100 g (0.616 mol) of triethyl orthoacetate (Note 2), and 0.24 g (3.2 mmol) of propionic acid. The solution is heated at 140–150°C in an oil bath. Every 2 hr, the ethanol produced is removed under reduced pressure with a rotary evaporator, and then 10 g (0.0562 mol) of triethyl orthoacetate and 0.024 g (0.32 mmol) of propionic acid are added. The mixture is heated until the starting material is consumed (6–8 hr) (Note 3). Excess triethyl orthoacetate is removed under reduced pressure (Note 4). The residue is distilled under reduced pressure to give 15.4–17.2 g (82–91%) of **1** (Note 5) as a clean oil, bp 80–85°C (0.3 mm).

B. *Ethyl (E,Z)-2,4-decadienoate* ***(2)***. A dry, 500-mL, round-bottomed flask is charged with 50 g of aluminum oxide (Note 6) and heated at 200°C for 2 hr under reduced pressure (0.05 mm). The flask is fitted with a reflux condenser connected to a nitrogen line and a heavy magnetic stirring bar is added (Note 7); the flask is flushed with nitrogen. With positive nitrogen pressure, the flask is charged with 200 mL of benzene (Note 8) and 15.4–17.2 g (78–88 mmol) of allenic ester **1**. The mixture is heated at reflux temperature with vigorous stirring for 5 hr. The aluminum oxide is removed by filtration with suction through a sintered-glass funnel of medium porosity and thoroughly washed with 100 mL of ethyl acetate (Note 9). The combined filtrate is concentrated with a rotary evaporator to afford 11.6–13.6 g (75–88%) of nearly pure **2** as a clean oil (Note 10) and (Note 11), bp 83–88°C (0.1 mm).

2. Notes

1. 1-Octyn-3-ol was used as supplied by Aldrich Chemical Company, Inc. (96% purity).
2. Triethyl orthoacetate was used as supplied by Aldrich Chemical Company, Inc. (97% purity) or by Tokyo Kasei Kogyo Co., Ltd. (98% purity).
3. The checkers removed the ethanol with a rotary evaporator and replaced it with fresh triethyl orthoacetate (10 g) and propionic acid (0.024 g) after 2, 4, and 6 hr.
4. The checkers removed excess triethyl orthoacetate under reduced pressure (0.05 mm) overnight. The recovered material may be easily purified by distillation and reused.
5. The product might contain trace amounts of triethyl orthoacetate, but it can be used for the next step since aluminum oxide adsorbs triethyl orthoacetate. The product[2] is characterized by IR (neat) cm^{-1}: 1970 and 1740; ^1H NMR (CCl_4) δ: 0.92 (t, 3 H, $CH_3(CH_2)_4$), 1.29 (t, 3 H, OCH_2CH_3), 1.32 (m, 6 H, $CH_3(CH_2)_3$), 1.91 (m, 2 H, $CH_2CH=$), 2.90 (m, 2 H, CH_2CO_2Et), 4.08 (q, 2 H, $CO_2CH_2CH_3$), 5.09 (m, 2 H, CH=C=CH).
6. Weakly basic alumina[3] (200–300 mesh) for column chromatography is used. The checkers used

Alumina Woelm-B, Akt. 1.

7. Efficient stirring is essential to the success of this reaction.

8. Aprotic solvents such as xylene, chlorobenzene, and toluene can be used instead of benzene. If the boiling point of the product is close to that of the solvent, the mixture of aluminum oxide and the allene may be heated to distil at ca. 150°C under an atmosphere of nitrogen.

9. The checkers found that the use of more than 100 mL of ethyl acetate gives a less pure final product.

10. Gas-chromatographic analysis (capillary column coated Thermon-1000, 30 m, 140°C) indicated that the product was ca. 93% pure. Impurities consisted of the 2*E*, 4*E* isomer (5%) and an unidentified compound (2%).

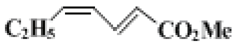
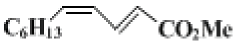
11. The proton magnetic resonance spectrum is as follows (CCl_4) δ: 0.90 (t, 3 H, *J* = 6, $CH_3(CH_2)_4$), 1.28 (t, 3 H, *J* = 7, $CO_2CH_2CH_3$), 1.40 (m, 6 H, $CH_3(CH_2)_3CH_2$), 1.9–2.6 (m, 2 H, $CH_2CH{=}CH$), 4.12 (q, 2 H, *J* = 7, $CO_2CH_2CH_3$), 5.4–6.3 (m, 3 H, $CH{=}CH\text{-}CH{=}CHCO_2Et$), 7.46 (dd, 1 H, *J* = 10 and 15, $CH{=}CHCO_2Et$); n_D^{25} 1.4895.

3. Discussion

Ethyl (*E,Z*)-2,4-decadienoate has been prepared in several ways: (a) the addition of lithium di-(*Z*)-1-heptenylcuprate to ethyl propiolate[4] [90% yield, 95% purity; 27–32% overall yield based on (*Z*)-1-bromoheptene],[5] (b) the reaction of 1-heptneylmagnesium bromide with ethyl (*E*)-β-(*N,N*-diethylamino) acrylate (32% yield, 89% purity),[6] and (c) the Wittig reaction of hexyltriphenylphosphonium bromide with ethyl (*E*)-4-oxo-2-butenoate (68% yield, 85% purity).[7] These known methods involving the use of organometallic reagents need anhydrous conditions at low temperatures (−8 to −40°C). Occasionally the separation of triphenylphosphine oxide from the reaction mixture in a Wittig reaction is not easy.

The present procedure offers an experimentally simple and less expensive preparation of ethyl (*E,Z*)-2,4-decadienoate under essentially neutral conditions. It allows large-scale preparation since the starting materials are not sensitive to air or moisture. In addition, the reaction proceeds stereoselectively, and the yields of product are generally high. Several examples are listed in Table I to show the scope of the method.

TABLE I
Rearrangement of β-Allenic Esters to (*E,Z*)-2,4-Dienoic Esters with Alumina[2]

Starting Material	Product	Yield (%)[a]	Purity (%)[b]
		57	90
		82	96
		80	96
		69	93
		87	93
		82	99
		87	91
		70	96

[a]Isolated yield.
[b]Purity determined by gas chromatography.

There are many compounds containing a conjugated (*E,Z*)-diene structure in naturally occurring compounds such as flavors,[3,8] insect pheromones,[3,9] and leukotrienes.[10] The present procedure has been used for the syntheses of bombykol,[3] megatomoic acid,[11] (±)-leukotriene A_4 methyl ester,[12] and (*E,Z*)-2,4-dienamides.[13]

References and Notes

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10. For example, see: Rokach, J.; Adams, J. *Acc. Chem. Res.* **1985**, *18*, 87; Hashimoto, S.; Toda, M. *Yuki Gosei Kagaku Kyokaishi* **1983**, *41*, 221; *Chem. Abstr.* **1983**, *98*, 191841*f*.
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

alumina

1-heptneylmagnesium bromide

ethanol (64-17-5)

Benzene (71-43-2)

ethyl acetate (141-78-6)

propionic acid (79-09-4)

nitrogen (7727-37-9)

chlorobenzene (108-90-7)

toluene (108-88-3)

xylene (106-42-3)

aluminum oxide (1344-28-1)

ethyl (E)-4-oxo-2-butenoate (2960-66-9)

triethyl orthoacetate (78-39-7)

ethyl propiolate (623-47-2)

(E,Z)-2,4-D (94-75-7)

triphenylphosphine oxide (791-28-6)

1-octyn-3-ol (818-72-4)

Ethyl 3,4-decadienoate (36186-28-4)

Ethyl (E,Z)-2,4-decadienoate,
2,4-Decadienoic acid, ethyl ester, (E,Z)- (3025-30-7)

hexyltriphenylphosphonium bromide (4762-26-9)

lithium di-(Z)-1-heptenylcuprate

(Z)-1-bromoheptene

ethyl (E)-β-(N,N-diethylamino)acrylate