



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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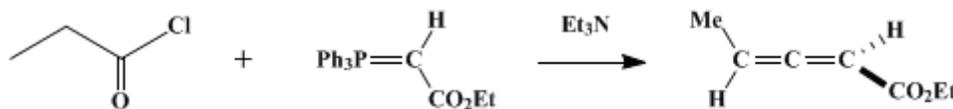
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 7, p.232 (1990); Vol. 62, p.202 (1984).

α -ALLENIC ESTERS FROM α -PHOSPHORANYLIDENE ESTERS AND ACID CHLORIDES: ETHYL 2,3-PENTADIENOATE

[2,3-Pentadienoic acid, ethyl ester]



Submitted by Robert W. Lang¹ and Hans-Jürgen Hansen².
Checked by William F. Burgoyne and Robert M. Coates.

1. Procedure

A 1-L, three-necked, round-bottomed flask is equipped with a nitrogen inlet, a 250-mL, pressure-equalizing dropping funnel fitted with a gas outlet, and a Teflon-coated magnetic stirring bar. The flask is charged with 300 mL of [dichloromethane](#) ([Note 1](#)) and 34.8 g (0.10 mol) of [ethyl \(triphenylphosphoranylidene\)acetate](#) ([Note 2](#)) and flushed with [nitrogen](#). The yellow solution is stirred at 25°C as a solution of 10.1 g (0.10 mol) of [triethylamine](#) ([Note 3](#)) in 100 mL of [dichloromethane](#) is added dropwise over 5 min. After 10 min, 9.25 g (0.10 mol) of [propionyl chloride](#) ([Note 4](#)) in 100 mL of [dichloromethane](#) is added dropwise to the vigorously stirred solution over 15 min ([Note 5](#)). Stirring is continued for an additional 0.5 hr ([Note 6](#)), after which the clear, yellow-tinted mixture is evaporated on a rotary evaporator at reduced pressure using a water bath maintained at 25°C ([Note 7](#)). A 500-mL portion of [pentane](#) ([Note 8](#)) is added to the semisolid residue, and the slurry is allowed to stand for 2 hr while it is shaken periodically to facilitate solidification and to complete the extraction of the product. The precipitate is removed by filtration through a coarse, sintered-glass Büchner funnel, and the filter cake is washed with a 50-mL portion of [pentane](#). The filtrates are combined and concentrated at reduced pressure to approximately one-fourth of the original volume using a water bath maintained at 25°C. The mixture is filtered again to remove [triphenylphosphine oxide](#), and the remaining solvent is then evaporated. Rapid distillation of the residual liquid in a short-path distillation apparatus under reduced pressure ([Note 9](#)) affords a small forerun amounting to 0.5 mL or less and 7.8–8.1 g (62–64%) of [ethyl 2,3-pentadienoate](#), bp 57–59°C (12–14 mm) ([Note 10](#)) and ([Note 11](#)).

2. Notes

- [Dichloromethane](#) was purified by percolation through Woelm activity grade 1 basic alumina and stored under [nitrogen](#).
- [Ethyl \(triphenylphosphoranylidene\)acetate](#) is available from Fluka AG and Tridom Chemical Inc. under the name [\(ethoxycarbonylmethylene\)triphenylphosphorane](#) and from Aldrich Chemical Company, Inc. under the name [\(carbethoxymethylene\)triphenylphosphorane](#). The reagent may be prepared from [triphenylphosphine](#) and [ethyl bromoacetate](#) by the following procedure.³
A 1-L, two-necked, round-bottomed flask fitted with a dropping funnel and a mechanical stirrer is charged with 131.0 g (0.5 mol) of [triphenylphosphine](#) (Fluka AG, purum) and 250 mL of [benzene](#) (Merck, pro analysi). The solution is stirred vigorously while 83.5 g (0.5 mol) of [ethyl bromoacetate](#) (Fluka AG, practical-grade) is added dropwise at a rate that maintains the reaction mixture at, or slightly above, room temperature. After a total of 2 hr the reaction is complete and the colorless phosphonium salt is filtered. The salt is washed with 300 mL of cold [benzene](#) and 200 mL of [pentane](#) and then dissolved in 3 L of water at room temperature. Some further organic impurities are removed by extraction with [ether](#), after which 2 drops of 2% alcoholic [phenolphthalein](#) are added. The aqueous solution is stirred vigorously and cooled in an ice bath as 2 M aqueous [sodium hydroxide](#) is added slowly until the pink endpoint is reached (pH 8–10). The crystalline [phosphorane](#) is collected by filtration, washed thoroughly with cold water, and dried, first with a rotary evaporator under reduced pressure at 60°C and then overnight in a drying oven at 180 mm and 70°C. The white to cream-colored crop of [ethyl \(triphenylphosphoranylidene\)acetate](#), mp 124–126°C, weighs 150–156 g (86–90%) and

may be used for the preparation of α -allenic esters without further purification.

3. **Triethylamine** was supplied by Fluka AG and Aldrich Chemical Company, Inc.

4. **Propionyl chloride** was purchased from Fluka AG and Aldrich Chemical Company, Inc. and was freshly distilled at 78–80°C (760 mm) prior to use.

5. The checkers maintained the temperature of the reaction mixture at ca. 25°C by cooling with a water bath during the addition of **propionyl chloride**.

6. The progress of the reaction may be followed by analytical thin-layer chromatography on alumina. The submitters used polygram precoated plastic sheets (Alox N/UV₂₅₄) purchased from Macherey-Nagel, Inc. The plates were developed with 1 : 1 **hexane** : **ether** and stained with basic permanganate. The retardation factor of the product is 0.56.

7. For the isolation of relatively volatile α -allenic esters such as **ethyl 2,3-pentadienoate**, the submitters recommend that the rotary evaporation be carried out with cooling in an ice bath. When this precaution was taken, the submitters obtained 8.5–9.5 g (67–75%) of product after distillation.

8. The checkers dried the **pentane** over **sodium wire** prior to use.

9. The checkers stirred the distilling liquid rapidly with a magnetic stirrer and maintained a bath temperature of 75–85°C throughout the distillation.

10. **Ethyl 2,3-pentadienoate** has the following spectral properties: IR (thin film) cm⁻¹: 1965, 1720, 1410, 1250, 1025, 865, 790; ¹H NMR (CCl₄) δ : 1.26 (t, 3 H, *J* = 7, OCH₂CH₃), 1.78 (m, 3 H, CH₃), 4.11 (q, 2 H, *J* = 7, OCH₂CH₃), 5.28–5.68 (m, 2 H, at C-2 and C-4).

11. On 0.01-mol scale the yield of **ethyl 2,3-pentadienoate** is 0.79–0.93 g (64–74%). The product was purified by bulb-to-bulb distillation with a Kugelrohr apparatus at 12–14 mm with an oven temperature at 75–85°C.

3. Discussion

The acylation of Wittig reagents provides the most convenient means for the preparation of allenes substituted with various electron-withdrawing substituents.⁴ The preparation of α -allenic esters has been accomplished by the reaction of resonance-stabilized phosphoranes with isolable ketenes^{5,6,7,8,9,10} and ketene itself¹ and with acid chlorides in the presence of a second equivalent of the **phosphorane**.⁶ The disadvantages of the first method are the necessity of preparing the ketene and the fact that the highly reactive monosubstituted ketenes evidently cannot be used. The second method fails when the α -carbon of the **phosphorane** is unsubstituted.¹²

TABLE I
PREPARATION OF α -ALLENIC ESTERS BY THE WITTIG REACTION¹³

R ¹	R ²	R ³	R ⁴	Solvent	Procedure ^a	Yield (%)
$(\text{Ph}_3\text{P})=\text{C}(\text{R}^2)\text{CO}_2\text{R}^1 + \begin{array}{c} \text{R}^4 \\ \\ \text{C}=\text{O} \\ \\ \text{R}^3 \quad \text{Cl} \end{array} \xrightarrow{\text{Et}_3\text{N}} \begin{array}{c} \text{R}^4 \\ \\ \text{R}^3\text{C}=\text{C}=\text{C} \\ \\ \text{CO}_2\text{R}^1 \end{array}$						
CH ₃	H	H	H	CH ₂ Cl ₂	A	$(\text{Ph}_3\text{P})=\text{C}(\text{H})\text{CO}_2\text{CH}_3 + \begin{array}{c} \text{H} \\ \\ \text{C}=\text{O} \\ \\ \text{H} \quad \text{Cl} \end{array} \xrightarrow{\text{Et}_3\text{N}} \begin{array}{c} \text{H} \\ \\ \text{H}\text{C}=\text{C}=\text{C} \\ \\ \text{CO}_2\text{CH}_3 \end{array}$ <p style="text-align: center;">40</p>
C ₂ H ₅	H	(CH ₃) ₃ C	H	CH ₃ CN	B	$(\text{Ph}_3\text{P})=\text{C}(\text{H})\text{CO}_2\text{C}_2\text{H}_5 + \begin{array}{c} \text{H} \\ \\ \text{C}=\text{O} \\ \\ (\text{CH}_3)_3\text{C} \quad \text{Cl} \end{array} \xrightarrow{\text{Et}_3\text{N}} \begin{array}{c} \text{H} \\ \\ (\text{CH}_3)_3\text{C}\text{C}=\text{C}=\text{C} \\ \\ \text{CO}_2\text{C}_2\text{H}_5 \end{array}$ <p style="text-align: center;">55</p>
CH ₃	H	C ₆ H ₅	H	CH ₃ CN	B	$(\text{Ph}_3\text{P})=\text{C}(\text{H})\text{CO}_2\text{CH}_3 + \begin{array}{c} \text{H} \\ \\ \text{C}=\text{O} \\ \\ \text{C}_6\text{H}_5 \quad \text{Cl} \end{array} \xrightarrow{\text{Et}_3\text{N}} \begin{array}{c} \text{H} \\ \\ \text{C}_6\text{H}_5\text{C}=\text{C}=\text{C} \\ \\ \text{CO}_2\text{C} \end{array}$ <p style="text-align: center;">23</p>

Switzerland. Work done at the Institute of Organic Chemistry, University of Fribourg, CH-1700 Fribourg, Péroilles, and supported by the Swiss National Science Foundation.

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

alumina

Benzene (71-43-2)

ether (60-29-7)

acetonitrile (75-05-8)

sodium hydroxide (1310-73-2)

nitrogen (7727-37-9)

sodium wire (13966-32-0)

Pentane (109-66-0)

dichloromethane (75-09-2)

phenolphthalein (77-09-8)

propionyl chloride (79-03-8)

Ethyl bromoacetate (105-36-2)

hexane (110-54-3)

triethylamine (121-44-8)

triphenylphosphine (603-35-0)

triphenylphosphine oxide (791-28-6)

betaine (107-43-7)

phosphorane (7723-14-0)

Ethyl 2,3-pentadienoate,
2,3-Pentadienoic acid, ethyl ester (74268-51-2)

ethyl (triphenylphosphoranylidene)acetate,
(ethoxycarbonylmethylene)triphenylphosphorane,
(carbethoxymethylene)triphenylphosphorane (1099-45-2)

oxaphosphetane