Organic Syntheses

A Publication
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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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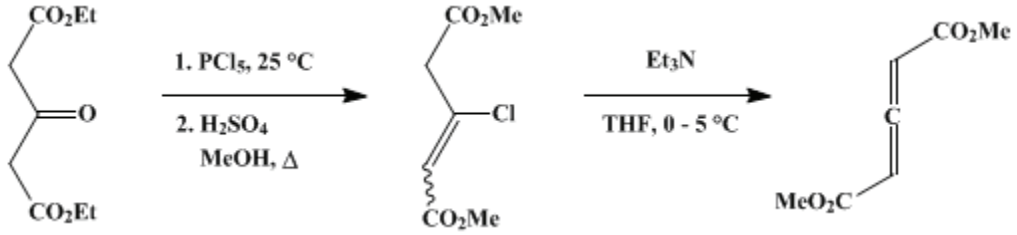
DIMETHYL 2,3-PENTADIENEDIOATE

[2,3-Pentadienedioic acid, dimethyl ester]



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1. Procedure

Caution! The reaction of phosphorus pentachloride with diethyl acetone-1,3-dicarboxylate should be carried out in a hood, since hydrogen chloride is evolved.

A. *Dimethyl 3-chloro-2-pentenedioate*. A dry, 500-ml., three-necked, round-bottomed flask fitted with a ground-glass stopper, a condenser provided with a gas bubbler, a gas-inlet adapter attached to a nitrogen (or argon) source, and a magnetic stirring bar, is charged with 60.0 g. (0.297 mole) of diethyl acetone-1,3-dicarboxylate (Note 1). A steady, gentle flow of nitrogen is started through the reaction vessel (Note 2), and 65.0 g. (0.313 mole) of phosphorus pentachloride (Note 3) is added in thirteen, approximately equal portions through the stoppered joint to the neat diester at 3-minute intervals with vigorous stirring (Note 4). After the addition is complete, the reaction mixture is warmed to 40° in a water bath for 30 minutes. The red solution is cooled in an ice bath and poured onto *ca.* 100 ml. of ice in a 500-ml. Erlenmeyer flask immersed in an ice bath. A 1 : 1 mixture of water and dichloromethane is used to rinse traces of the product from the reaction vessel into the Erlenmeyer flask, and the resulting mixture is stirred for 15 minutes (Note 5). After separating the two layers, the aqueous phase is extracted with three 100-ml. portions of dichloromethane, and the combined organic extracts are dried over anhydrous sodium sulfate. Filtration through glass wool and removal of solvents with a rotary evaporator affords *ca.* 60 g. of a red oil, which is placed in a 500-ml., round-bottomed flask containing 20 ml. of concentrated sulfuric acid in 300 ml. of anhydrous methanol (Note 6), and the solution is refluxed using a heating mantle for 18 hours. Excess methanol (200 ml.) is distilled, and the residual yellow solution is cooled to room temperature and poured into 100 ml. of water. Sodium chloride is added to saturation, and the solution is extracted with eight 100-ml. portions of diethyl ether. The combined extracts are washed successively with 150 ml. of aqueous saturated sodium hydrogen carbonate and 150 ml. of aqueous saturated sodium chloride, dried over anhydrous sodium sulfate, and filtered. Concentration of the extract with a rotary evaporator affords a yellow oil which is distilled, yielding 33.5–34.4 g. (59–60%) of dimethyl 3-chloro-2-pentenedioate[2] as a colorless liquid, b.p. 50–60° (0.02 mm.) (Note 7).

B. *Dimethyl 2,3-pentadienedioate*. A 500-ml., three-necked, round-bottomed flask, equipped with a gas-inlet adapter, a 50-ml. addition funnel, a ground-glass stopper, and a magnetic stirring bar, is charged with 27.0 g. (0.145 mole) of the diester from Part A and 100 ml. of anhydrous tetrahydrofuran (freshly distilled from sodium). The flask is flushed with nitrogen (or argon), and a positive pressure is maintained while the contents are cooled to 0° in an ice–salt bath and stirred with an efficient motor. Triethylamine (22 ml., 0.16 mole, freshly distilled from calcium hydride) is added through the addition funnel over a 10-minute period, the gas-inlet adapter is replaced with a calcium chloride tube, and the mixture is stirred at 0–5° for 18 hours (Note 8). The precipitate is removed by vacuum filtration and washed with three 100-ml. portions of anhydrous diethyl ether. The combined filtrate and washings are

washed successively with three 75-ml. portions of 0.1 *N* hydrochloric acid and 100 ml. of aqueous saturated sodium chloride, dried over anhydrous sodium sulfate, filtered, and concentrated with a rotary evaporator. The residual oil is distilled (Note 9), yielding 13.3–13.9 g. (61–64%) of dimethyl 2,3-pentadienedioate[3] (Note 10), b.p. 58° (0.02 mm.).

2. Notes

1. Diethyl acetone-1,3-dicarboxylate was purchased from the Aldrich Chemical Company, Inc., and the checkers distilled this material under reduced pressure, b.p. 135–137° (12 mm.), discarding *ca.* 10% as a forerun.
2. A continuous flow of inert gas removes hydrogen chloride and phosphoryl chloride from the reaction flask.
3. Phosphorus pentachloride was purchased by the checkers from the J. T. Baker Chemical Company, and purchased from Eastman Organic Chemicals by the submitters.
4. Warming and foaming occur during the addition, and the temperature reaches *ca.* 40–45°.
5. The checkers found that unless the aqueous workup is cooled, the dichloromethane boils vigorously.
6. The checkers used commercial "anhydrous" methanol without further drying.
7. The checkers determined the product to be a mixture of isomers (approximately 6 : 1) by GC analysis (15% SE-30 on Chromosorb W, 0.3 × 244 cm., 175°) and by ^{1}H NMR. The mixture was characterized as follows: IR (liquid film) cm.$^{-1}$: 1745 strong (shoulder at 1720), 1640 medium strong, 1440 medium strong; ^{1}H NMR ($CDCl_3$), δ (multiplicity, number of protons): 3.75 (s, 6H), 4.12 (s, 2H), 6.21 (s, 1H), and 6.30 (s, 1H).
8. During this time a heavy precipitate of triethylamine hydrochloride forms; the mixture first becomes yellow and eventually brown in color.
9. The allene apparently polymerizes during distillation; it yellows in the receiving flask, and becomes orange and viscous even in the refrigerator overnight. The submitters obtained higher yields by distilling the product in batches.
10. The checkers characterized the product as follows: IR (liquid film) cm.$^{-1}$: 1970 strong, 1720 strong, 1440 strong; ^{1}H NMR ($CDCl_3$), δ (multiplicity, number of protons): 3.81 (s, 6H), 6.10 (s, 2H).

3. Discussion

Dimethyl 2,3-pentadienedioate has also been prepared from the enol phosphate of diethyl acetone-1,3-dicarboxylate.[4]

References and Notes

1. Department of Chemistry, University of South Carolina, Columbia, S.C. 29208.
2. J. M. van der Zandon, *Recl. Trav. Chim. Pays-Bas*, **54**, 289 (1935).
3. G. Büchi and J. Carlson, *J. Am. Chem. Soc.*, **91**, 6470 (1969).
4. J. Craig and J. Moyle, *J. Chem. Soc.*, 5356 (1963).

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

enol phosphate of diethyl acetone-1,3-dicarboxylate

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

methanol (67-56-1)

diethyl ether (60-29-7)

phosphorus pentachloride (10026-13-8)

sodium hydrogen carbonate (144-55-8)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

sodium (13966-32-0)

diethyl acetone-1,3-dicarboxylate (105-50-0)

Triethylamine hydrochloride (554-68-7)

dichloromethane (75-09-2)

Tetrahydrofuran (109-99-9)

triethylamine (121-44-8)

argon (7440-37-1)

calcium hydride (7789-78-8)

Dimethyl 2,3-pentadienedioate,
2,3-Pentadienedioic acid, dimethyl ester (1712-36-3)

Dimethyl 3-chloro-2-pentenedioate (66016-88-4)

phosphoryl chloride (10025-87-3)