



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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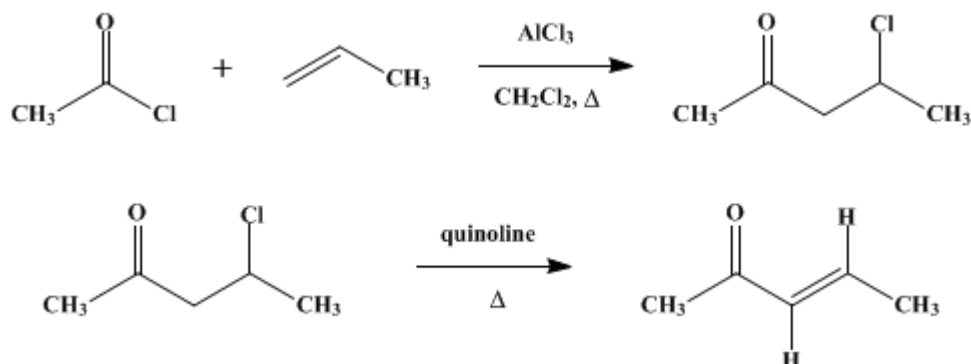
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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***trans*-3-PENTEN-2-ONE**

[3-Penten-2-one, *trans*-]



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Checked by Walter J. Campbell and Herbert O. House.

1. Procedure

Caution! Since both hydrogen chloride and propene may escape from the reaction vessel during this preparation, the reaction should be performed in a hood.

A 2-l., three-necked flask is equipped with an efficient mechanical stirrer, a gas-inlet tube extending almost to the bottom of the flask, and an efficient reflux condenser fitted with a calcium chloride drying tube. After the apparatus has been dried in an oven, 800 ml. of dichloromethane (Note 1) and 157 g. (142 ml., 2.00 moles) of acetyl chloride (Note 2) are added to the flask. This solution is stirred while 320 g. (2.40 moles) of powdered, anhydrous aluminum chloride (Note 3) is added in portions over a 15-minute period. As soon as this addition is complete, a stream of propene gas (Note 4) is passed through the continuously stirred reaction solution at a rate sufficient to maintain a gentle reflux. The gas flow is continued until no more heat is evolved and refluxing ceases (10–30 hours, (Note 4), at which time the flask is nearly full and the contents separate into two layers after stirring is stopped. The contents of the flask are poured cautiously onto about 1.5 kg. of ice (Note 5), and the upper organic layer is separated. The aqueous phase is shaken with three 100-ml. portions of dichloromethane (Note 6), and the combined organic solutions are washed with 50 ml. of water and dried over anhydrous magnesium sulfate.

The resulting dark brown solution is placed in a 2-l., round-bottomed flask equipped with a thermometer, a magnetic stirring bar, a heating mantle, and an assembly consisting of a distilling head, a condenser, and a receiver which permits distillation under reduced pressure. The bulk of the dichloromethane and volatile hydrocarbons are distilled from the mixture at water-aspirator pressure while sufficient heat is supplied with the heating mantle, maintaining the temperature of the mixture at about 0° (Note 7). When the bulk of the solvent has been removed, a 1-l., round-bottomed flask, cooled in a 2-propanol–dry ice bath, is attached to the apparatus as a receiver, and the pressure is reduced to 1 mm. or less with a vacuum pump. With the heating mantle, the temperature of the viscous liquid in the distillation flask is raised slowly from about 0° to 45° over a period of 90 minutes, distilling the volatile products (dichloromethane, low molecular-weight hydrocarbons, 4-chloropentan-2-one, and 3-penten-2-one) (Note 7). The resulting distillate (400–500 g. of pale green liquid) is mixed with 256 g. (1.98 moles) of quinoline (Note 8) and heated to boiling. To remove the remaining dichloromethane and other low-boiling materials (Note 9), liquid is allowed to distil from the mixture until the temperature of the distilling liquid reaches 110–120°. The remaining solution is refluxed for 30 minutes, then cooled and diluted with the previously removed distillate and 200 ml. of pentane. The resulting solution is washed

with successive 250-ml. portions of 10% hydrochloric acid until the aqueous washings are acidic. The aqueous washings are combined, acidified, and shaken with three 100-ml. portions of pentane. The combined organic solutions are washed with 50 ml. of saturated aqueous sodium hydrogen carbonate and dried over anhydrous magnesium sulfate. The resulting organic solution is fractionally distilled through a 30-cm. Vigreux column, and 42–63 g. (25–37%) of crude product is collected in the fraction boiling at 119–124°. This contains 3-penten-2-one of 86–92% purity (Note 10). If greater purity is desired, the crude product may be distilled through a 60-cm., spinning band column. Since this distillation may be accompanied by partial isomerization of the α,β -unsaturated ketone to the lower boiling β,γ -isomer (Note 10), the product from the fractional distillation should be subjected to an acid-catalyzed equilibration. In a typical purification 79.4 g. of a mixture of penten-2-one isomers, b.p. 117–119°, from a fractional distillation, is mixed with 400 mg. of *p*-toluenesulfonic acid and refluxed for 30 minutes. The resulting mixture is diluted with 100 ml. of diethyl ether and washed with 50 ml. of saturated aqueous sodium hydrogen carbonate and dried over anhydrous magnesium sulfate. The resulting ether solution is fractionally distilled through a 16-cm. Vigreux column, giving 60.4 g. of *trans*-3-penten-2-one of 97% purity, b.p. 121.5–124°, n_D^{25} 1.4329 (Note 11).

2. Notes

1. Dichloromethane was dried over calcium chloride before use.
2. The submitters used a practical grade of acetyl chloride obtained from Eastman Organic Chemicals. The checkers used reagent grade acetyl chloride obtained from the Industrial Chemicals Division, Allied Chemical Corporation.
3. The reagent grade of powdered, anhydrous aluminum chloride employed was obtained from the Specialty Chemicals Division, Allied Chemical Corporation.
4. A chemically pure grade of propene, obtained from Matheson Gas Products, was employed. A large excess of propene is used since much of the olefin is converted to polymeric products. The submitters report obtaining markedly lower yields of product when an excess of propene was not used.
5. At this point there should be only a relatively mild exothermic reaction as the anhydrous aluminum salts are hydrolyzed and solvated.
6. In these extractions the organic layer is the lower one.
7. The submitters had originally distilled the volatile products from this mixture, containing mainly polymeric material, by a more conventional procedure. However, the checkers found the problem of foaming during distillation so severe that the alternative, low-temperature distillation procedure was adopted.
8. The practical grade of quinoline employed was obtained from Aldrich Chemical Company, Inc.
9. The reaction solution must reach a temperature of approximately 90° for rapid dehydrochlorination to occur. If low-boiling impurities prevent the reaction mixture from reaching this temperature, the final product may be contaminated with the intermediate β -chloroketone. On a GC column packed with Carbowax 20M suspended on Chromosorb P, the retention times for the α,β -unsaturated ketone and the intermediate β -chloroketone are 4.9 minutes and 12.0 minutes, respectively. A sample of 4-chloro-2-pentanone, collected from this GC column, has IR absorption (CHCl_3) at 1720 cm^{-1} (C=O) with ^1H NMR absorption (CDCl_3) at δ 1.55 (d, $J = 7$ Hz., 3H, CH_3), 2.20 (s, 3H, CH_3CO), 2.5–3.3 (m, 2H, CH_2), and 4.45 (sextuplet, $J = 7$ Hz., 1H, CHCl).
10. The product was analyzed with a 2-m. GC column packed with Carbowax 20M suspended on Chromosorb P. In chromatograms obtained from this column at 100°, the retention times of 4-penten-2-one and 3-penten-2-one are 2.6 and 3.9 minutes, respectively. The crude product contains several additional low-boiling components with GC retention times in the range 1.6–2.8 minutes. Any 4-penten-2-one present as an impurity exhibits IR absorption (CCl_4) at 1720 cm^{-1} (nonconjugated C=O).
11. The pure *trans*-3-penten-2-one has IR absorption (CCl_4) at 1680 and 1705 cm^{-1} (cisoid and transoid conformers² of the conjugated C=O), 1635 cm^{-1} (conjugated C=C), and 970 cm^{-1} (*trans*-CH=CH) with a UV maximum (95% $\text{C}_2\text{H}_5\text{OH}$) at 220 nm (ϵ 11,000) and ^1H NMR absorption (CDCl_3) at δ 1.88 (d of d, $J = 1.5$ and 7 Hz., 3H, CH_3), 2.22 (s, 3H, CH_3CO), 6.10 (d of partially resolved m, $J = 16$ Hz., 1H, α -vinyl CH), and 6.85 (d of q, $J = 7$ and 16 Hz., 1H, β -vinyl CH). The mass spectrum of the product has the following relatively abundant peaks: m/e (relative intensity), 84(M^+ , 36), 69(100), 43(57), 41(78), and 39(33).

3. Discussion

trans-3-Penten-2-one has been prepared by the dehydration of 4-hydroxy-2-pentanone with heat,³ acetic anhydride,³ sulfuric acid,⁴ or iodine.⁵ It has also been obtained by fractional distillation of a commercial product from the aldol condensation of acetaldehyde and acetone.⁶ Preparations are described involving reactions of acetyl bromide with propene, in the presence of anhydrous aluminum bromide,⁷ and of acetic anhydride or acetyl chloride with propene, in the presence of anhydrous aluminum chloride.⁸ Other preparative methods include the oxidation of *trans*-3-penten-2-ol with chromic acid⁶ and the Wittig reaction between acetylmethylenetriphenylphosphorane and acetaldehyde.⁹

The present procedure, an adaptation of one described previously,⁸ illustrates the acylation of an olefin in the presence of a Lewis-acid catalyst. Although this method may lead to complex mixtures of acylated products when higher molecular-weight olefins are acylated in the presence of excess aluminum chloride, the application of this procedure to propene gives a single, monomeric, acetylated product, accompanied by a complex mixture of low molecular-weight hydrocarbons and unidentified, higher molecular-weight materials. The relatively low boiling point of the monoacetylated product permits its ready separation from most of the components of this mixture, after which it is dehydrochlorinated to the desired product. The product of this reaction is of sufficient purity to serve as a synthetic intermediate in annelation reactions with cycloalkanones.¹⁰

References and Notes

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10. See, for example, J. A. Marshall, H. Faubl, and T. M. Warne, Jr., *Chem. Commun.*, 753 (1967); R. M. Coates and J. E. Shaw, *Chem. Commun.*, 47 (1968); H. C. Odom and A. R. Pinder, *J. Chem. Soc. Chem. Commun.*, 26 (1969); J. A. Marshall and R. A. Ruden, *Tetrahedron Lett.*, 1239 (1970).

Appendix

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

calcium chloride (10043-52-4)

acetaldehyde (75-07-0)

sulfuric acid (7664-93-9)

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

ether,
diethyl ether (60-29-7)

acetic anhydride (108-24-7)

acetyl chloride (75-36-5)

sodium hydrogen carbonate (144-55-8)

Propene (115-07-1)

iodine (7553-56-2)

acetone (67-64-1)

aluminum chloride (3495-54-3)

chromic acid (7738-94-5)

Quinoline (91-22-5)

Pentane (109-66-0)

aluminum bromide

dichloromethane (75-09-2)

magnesium sulfate (7487-88-9)

acetyl bromide (506-96-7)

4-hydroxy-2-pentanone

3-penten-2-one (625-33-2)

p-toluenesulfonic acid (104-15-4)

4-chloropentan-2-one,
4-chloro-2-pentanone

4-penten-2-one

acetylmethylenetriphenylphosphorane

trans-3-Penten-2-one,
3-Penten-2-one, trans- (3102-33-8)

trans-3-penten-2-ol

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