



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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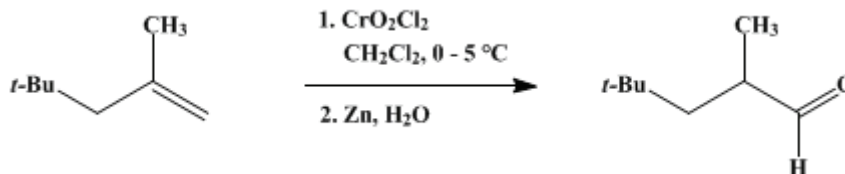
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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ALDEHYDES BY OXIDATION OF TERMINAL OLEFINS WITH CHROMYL CHLORIDE: 2,4,4-TRIMETHYLPENTANAL

[Pentanal, 2,4,4-trimethyl-]



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1. Procedure

A 5-l., three-necked flask fitted with a mechanical stirrer, a thermometer, and a dropping funnel equipped with a calcium chloride drying tube is charged with 112.2 g. (1.002 mole) of freshly distilled 2,4,4-trimethyl-1-pentene (Note 1) and 1 l. of dichloromethane (Note 2). The flask is immersed in an ice-salt bath, and the stirred solution is cooled to 0–5°. A solution of 158 g. (1.02 moles) (Note 3) of freshly distilled chromyl chloride (Note 4) in 200 ml. of dichloromethane (Note 5) is added dropwise with stirring from the dropping funnel while the temperature is maintained at 0–5° (Note 6). The reaction mixture is stirred for 15 minutes, and 184 g. of 90–95% technical grade zinc dust (Note 7) is added. The mixture is stirred for 5 minutes, 1 l. of ice water and 400 g. of ice are added as rapidly as possible (Note 8), and the mixture is stirred for an additional 15 minutes. The ice-salt bath is replaced with a heating mantle, and the flask is fitted for steam distillation. After distillation of the dichloromethane the residue is steam distilled (Note 9). The distillate is transferred to a separatory funnel, the organic layer is separated, and the aqueous layer is washed with three 50-ml. portions of dichloromethane. The combined organic phases are distilled (Note 10) through a 56-cm., vacuum-jacketed, Vigreux column, removing the solvent. The product is transferred to a 250-ml. round-bottomed flask and distilled. After removal of a small amount of dichloromethane the fraction boiling at 45–52° (15 mm.) is collected, giving 90–100 g. (70–78%) (Note 11) of 2,4,4-trimethylpentanal.

2. Notes

1. The alkene is available from Aldrich Chemical Company, Inc., or Phillips Petroleum Company, and can be used without distillation.
2. The material available from Matheson, Coleman and Bell or Eastman Organic Chemicals is satisfactory except as explained in (Note 5).
3. Since chromyl chloride is easily hydrolyzed, a slight excess is used.
4. The fraction, b.p. 115.5–116.5°, is used. Chromyl chloride is available from Alfa Inorganics, Inc.
5. Chromyl chloride tends to react slowly with the commercially available dichloromethane. This can be avoided with a slight increase in yield if the dichloromethane used to dissolve the chromyl chloride is distilled through a 15–20 cm. Vigreux column immediately before use.
6. The time required for the addition is about 60 minutes.
7. This approximate fivefold excess is necessary to reduce the higher valence chromium salts, thereby eliminating overoxidation and double bond cleavage. The zinc dust used was obtained from Allied Chemical Corporation.
8. The temperature usually increases to 8–10°.
9. Steam distillation is discontinued when the distillate gives a negative test with 2,4-dinitrophenylhydrazine.
10. It is not necessary to dry the organic phase.
11. The checkers, working at two-thirds scale, obtained the product in 70–71% yield.

3. Discussion

2,4,4-Trimethylpentanal has been prepared by the catalytic isomerization of 1,2-epoxy-2,4,4-trimethylpentane in both the liquid and gas phases (77–92%),² and by the oxidation of 2,4,4-trimethyl-1-pentene with chromium trioxide in acetic anhydride.³ Although the catalytic isomerization of the epoxide² gives 2,4,4-trimethylpentanal in good yield, this requires epoxidation of the alkene as the first step. The chromyl acetate and chromic acid oxidative methods give unsatisfactory yields.³ In the preparation described here, 2,4,4-trimethylpentanal is obtained from the alkene in good yield, in one step. Also, this preparation illustrates a general and convenient procedure for the direct oxidation of 2,2-disubstituted-1-alkenes (Table I) to unstable and reactive aldehydes.⁴ The reaction is very fast and the aldehyde is the major product.

TABLE I
ALDEHYDES BY OXIDATION OF TERMINAL OLEFINS WITH CHROMYL
CHLORIDE

Alkene	Aldehyde	Yield, %
4,4-Dimethyl-2-neopentyl-1-pentene	4,4-Dimethyl-2-neopentylpentanal	80.8 ^a
2-Phenylpropene	2-Phenylpropanal	60.0 ^b
1,1-Diphenylethylene	Diphenylacetaldehyde	62.7 ^b

^aReference ⁴.

^bReference ⁵.

4,4-Dimethyl-2-neopentylpentanal,⁶ 2-phenylpropanal,⁷ and Diphenylacetaldehyde⁸ are generally prepared by isomerization of the corresponding epoxide and/or by multistep syntheses.

In contrast to the relative simplicity of the chromyl chloride oxidation of 2,2-disubstituted-1-alkenes to aldehydes, the chromyl acetate and chromic acid oxidations generally lead to epoxides, acids, and carbon-carbon double bond cleavage. For example, chromyl acetate oxidizes 4,4-dimethyl-2-neopentyl-1-pentene primarily to 1,2-epoxy-4,4-dimethyl-2-neopentylpentane in low yield,⁹ and chromic acid oxidizes the alkene principally to 4,4-dimethyl-2-neopentylpentanoic acid.^{6,10}

References and Notes

1. Department of Chemistry, California State College, Long Beach, California 90801. This investigation was supported by the Long Beach California State College Foundation, the Research Corporation, and the Petroleum Research Fund administered by the American Chemical Society. [Present address: Department of Chemistry, University of California, Irvine, California 92717].
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

acetic anhydride (108-24-7)

zinc (7440-66-6)

chromic acid (7738-94-5)

1,1-Diphenylethylene (530-48-3)

2,4-Dinitrophenylhydrazine (119-26-6)

dichloromethane (75-09-2)

chromyl chloride

chromium trioxide (1333-82-0)

2-phenylpropanal (93-53-8)

Diphenylacetaldehyde (947-91-1)

2-Phenylpropene (98-83-9)

2,4,4-Trimethylpentanal,
Pentanal, 2,4,4-trimethyl- (17414-46-9)

2,4,4-trimethyl-1-pentene (107-39-1)

1,2-epoxy-2,4,4-trimethylpentane

chromyl acetate

4,4-Dimethyl-2-neopentylpentanal

4,4-Dimethyl-2-neopentyl-1-pentene (141-70-8)

1,2-epoxy-4,4-dimethyl-2-neopentylpentane

4,4-dimethyl-2-neopentylpentanoic acid