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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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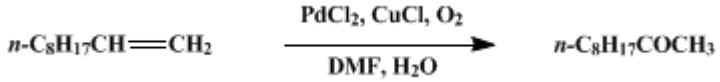
A GENERAL SYNTHETIC METHOD FOR THE PREPARATION OF METHYL KETONES FROM TERMINAL OLEFINS: 2-DECANONE



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1. Procedure

A 100-mL, three-necked, round-bottomed flask is fitted with a magnetic stirrer and a pressure-equalizing dropping funnel containing 1-decene (4.2 g, 30 mmol). The flask is charged with a mixture of palladium chloride (0.53 g, 3 mmol), cuprous chloride (2.97 g, 30 mmol) (Note 1), and aqueous dimethylformamide (DMF/H_2O = 7:1, 24 mL). With the other outlets securely stoppered and wired down, an oxygen-filled balloon (Note 2) is placed over one neck, and the flask is stirred at room temperature to allow oxygen uptake (Note 3). After 1 hr, 1-decene (4.2 g, 30 mmol) (Note 4) is added over 10 min (Note 5) using the dropping funnel, and the solution is stirred vigorously at room temperature under an oxygen balloon (Note 6). The color of the solution turns from green to black within 15 min and returns gradually to green. After 24 hr, the mixture is poured into cold 3 *N* hydrochloric acid (100 mL) and extracted with five 50-mL portions of ether. The extracts are combined and washed successively with 50 mL of saturated sodium bicarbonate solution, 50 mL of brine, and then dried over anhydrous magnesium sulfate. After filtration, the solvent is removed by evaporation and the residue is distilled using a 15-cm Vigreux column to give 2-decanone as a colorless oil (3.0–3.4 g, 65–73%, bp 43–50°C/1 mm (Note 7) and (Note 8).

2. Notes

1. Cupric chloride can be used, but it tends to chlorinate the products and cuprous chloride is preferable; reagent-grade dimethylformamide (DMF) was distilled before use.
2. The balloon was purchased at a toy shop; its inflated volume was approximately 500 mL.
3. The initial black solution gradually turns green by oxygen absorption.
4. The sample of 1-decene was obtained from the Aldrich Chemical Company, Inc. and distilled before use.
5. In cases where the alkene is soluble, up to 30% of the aqueous DMF can be mixed with the alkene to facilitate controlled addition. With 1-decene, DMF forms a two-phase mixture.
6. The reaction is slightly exothermic.
7. The first fraction (bp 30–40°C) contains decenes that are formed by palladium-catalyzed isomerization of 1-decene (indicated by a broad signal at δ 5.2–5.5 in the ^{1}H NMR spectrum).
8. The spectral properties of 2-decanone are as follows: ^{1}H NMR (CCl_4) δ: 0.7–1.8 (15 H, complex), 2.02 (3 H, s), 2.37 (2 H, t, J = 7); IR (neat) 1722 cm^{-1}.

3. Discussion

Methyl ketones are important intermediates for the synthesis of methyl alkyl carbinols, annulation reagents, and cyclic compounds. A common synthetic method for the preparation of methyl ketones is the alkylation of acetone derivatives, but the method suffers limitations such as low yields and lack of regioselectivity. Preparation of methyl ketones from olefins and acetylenes using mercury compounds is a better method. For example, hydration of terminal acetylenes using $HgSO_4$ gives methyl ketones cleanly.[2] Oxymercuration of 1-olefins and subsequent oxidation with chromic oxide is another method.[3] Preparation of an epoxide from a 1-olefin and its rearrangement catalyzed by a cobalt catalyst to give methyl ketones has been reported briefly.[4]

Compared with these methods, the palladium-catalyzed oxidation of 1-olefins described here is more convenient and practical. The industrial method of ethylene oxidation to acetaldehyde using $PdCl_2$–$CuCl_2$–O_2 is the original reaction of this type.[5] The oxidation of various olefins has been carried out.[6,7,8,9]

Use of DMF as a solvent for the oxidation of 1-olefins has been reported by Clement and Selwitz.[6] The method requires only a catalytic amount of $PdCl_2$ and gives satisfactory yields under mild conditions. A small amount of olefin migration product is the only noticeable contaminant in the cases reported. The procedure can be applied satisfactorily to various 1-olefins with other functional groups. This useful synthetic method for the preparation of methyl ketones has been applied extensively in the syntheses of natural products such as steroids,[10] macrolides,[11,12] dihydrojasmone,[13] and muscone.[14] A comprehensive review article on the palladium-catalyzed oxidation of olefins has been published.[15]

References and Notes

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

mercury compounds

METHYL KETONES

dimethylformamide (DMF)

acetaldehyde (75-07-0)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium bicarbonate (144-55-8)

oxygen (7782-44-7)

cuprous chloride (7758-89-6)

cupric chloride (7758-89-6)

palladium chloride (7647-10-1)

magnesium sulfate (7487-88-9)

dimethylformamide (68-12-2)

cobalt (7440-48-4)

chromic oxide (1308-38-9)

2-Decanone (693-54-9)

1-decene (872-05-9)