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A Convenient Synthesis of 2-Cyclopentenone

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A convenient and practical synthesis of 2-cyclopentenone has been developed.

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2-Cyclopentenone (**6**) serves as a versatile starting material for a wide variety of compounds owing to its reactive α, β-unsaturated carbonyl system in the five membered ring. Despite the simple structure of **6**, known synthetic methods are not convenient for preparative use.[1] In this paper we describe a convenient synthesis based on the method developed by DePuy and Eilers.[1] In their synthesis, 2-cyclopentenone (**6**) was prepared by acid-catalyzed dehydration of a mixture of isomeric cyclopentenediols[2] which was synthesized from cyclopentadiene (**2**) by oxidation with 40% peracetic acid. In the present synthesis, we used a mixture of *cis*- and *trans*-4-*tert*-butoxy-[3] (**4a**) or 4-cumyloxy-[4] (**4b**) 2-cyclopenten-1-yl acetates as a starting material which could be obtained more safely from cyclopentadiene (**2**) by using *tert*-butyl hydroperoxide[3] or cumyl hydroperoxide[4] as the oxidant. The acetoxy ethers (**4**) were converted into the corresponding hydroxy ethers (**5**) in excellent yields on methanolysis in the presence of potassium carbonate[5] or on alkaline hydrolysis.[4] Upon treatment with a catalytic amount of *p*-toluenesulfonic acid[1] the *tert*-butyl (**5a**) and the cumyl (**5b**) ethers gave 2-cyclopentenone (**6**) in 55 and 76% yields, respectively.

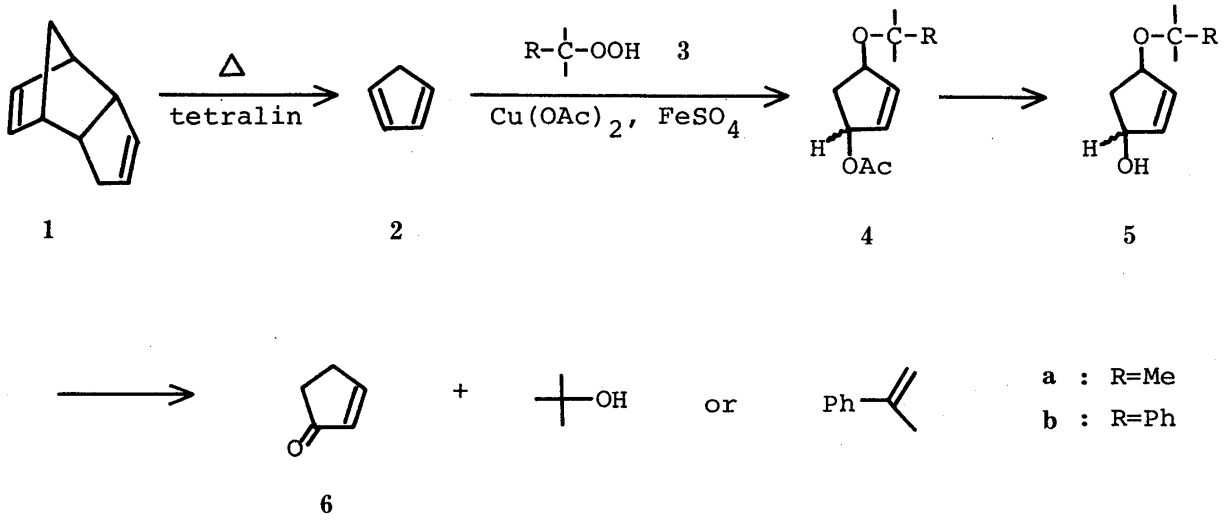

Chart 1

Experimental

All reactions were carried out under argon. Infrared (IR) spectra were recorded on a JASCO A-220 spectrophotometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded with a JEOL-PMX 60 spectrometer.

A Mixture of *cis*- and *trans*-4-Cumyloxy-2-cyclopenten-1-yl Acetate (4b)——A solution of iron (II) sulfate (722.9 g, 2.6 mol) in water (1360 ml) was added dropwise to a stirred suspension of cyclopentadiene (**2**) (171.9 g, 2.6 mol, freshly prepared from dicyclopentadiene),$^{6)}$ cumyl hydroperoxide (80% in cumene)$^{7)}$ (500 g, 2.6 mol), and copper (II) acetate (519 g, 2.6 mol) in acetic acid (580 ml), while keeping the reaction temperature below 10 °C with cooling. After the addition, the mixture was further stirred for 3 h at room temperature and then extracted with methylene chloride (3000 ml). The extract was washed successively with water, saturated aqueous sodium hydrogen carbonate, and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent left a brown oil, which was distilled under vacuum to give a mixture (1 : 2) of *cis*- and *trans*-4-cumyloxy-2-cyclopentenol acetate (**4b**) (358.3 g, 53%) as a colorless oil: bp 130—135 °C (0.1 mmHg). IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 1730. ^{1}H-NMR (CDCl$_3$) δ: 1.6 (6H, s, $C(C\underline{H}_3)_2Ph$), 1.96 (1H, s, $COC\underline{H}_3$), 2.02 (2H, s, $COC\underline{H}_3$), 1.8—3.0 (2H, m, $C\underline{H}_2$), 4.0—4.3 (1/3H, m, $C\underline{H}O$), 4.35—4.65 (2/3H, m, $C\underline{H}O$), 5.2—5.6 (1/3H, m, $C\underline{H}OAc$), 5.6—5.8 (2/3H, m, $C\underline{H}OAc$), 5.85—6.0 (2H, m, $C\underline{H}=C\underline{H}$), 7.2—7.6 (5H, m, Ph). MS *m/z*: 260 (M$^+$), 119 (100%).

A Mixture of *cis*- and *trans*-4-*tert*-Butoxy-2-cyclopentenol (5a)——A mixture of the acetate (**4a**) (79.2 g, 0.40 mol) in ethanol (300 ml) and potassium carbonate (27.6 g, 0.20 mol) was stirred at room temperature for 24 h. The mixture was filtered by using Celite, and the filtrate was concentrated under reduced pressure. The residue was diluted with methylene chloride (500 ml), washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent left a brown oil, which was distilled under vacuum to give the alcohol (**5a**) (55.9 g, 89.7%) as a colorless oil; bp 55—60 °C (0.15 mm Hg). IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 3300. ^{1}H-NMR (CDCl$_3$) δ: 1.20 (9H, s, $C(C\underline{H}_3)_3$), 1.30—3.10 (3H, $C\underline{H}_2$, $CHO\underline{H}$), 4.33—4.72 (3/2H, m, $C\underline{H}O$), 4.70—5.13 (1/2 H, m, $C\underline{H}OH$), 5.67—6.00 (2H. m, $C\underline{H}=C\underline{H}$). MS *m/z*: 156 (M$^+$), 57 (100%). *Anal.* Calcd for $C_9H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.56; H, 11.34.

A Mixture of *cis*- and *trans*-4-Cumyloxy-2-cyclopentenol (5b)——A mixture of the acetate (**4b**) (80 g, 0.307 mol) in ethanol (500 ml) and 10% aqueous potassium hydroxide (500 ml) was stirred at room temperature for 1 h. After evaporation of most of the ethanol under reduced pressure, the aqueous residue was extracted with methylene chloride (500 ml) and the extract was washed with brine and dried over anhydrous magnesium sulfate. The extract was evaporated *in vacuo* and the residue was distilled under vacuum to give the alcohol (**5b**) (57.3 g, 85.6%) as a colorless oil; bp 115—120 °C (0.3 mmHg). IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 3400. ^{1}H-NMR (CDCl$_3$) δ: 1.6 (6H, s, $C(C\underline{H}_3)_2Ph$), 1.8—3.0 (3H, m, $C\underline{H}_2$, $O\underline{H}$ (exchangeable)), 3.6—3.8 (1/3H, m, $C\underline{H}OH$), 4.0—4.2 (2/3H, m, $C\underline{H}OH$), 4.4—4.7 (2/3H, m, $C\underline{H}O$), 4.9—5.1 (1/3H, m, $C\underline{H}O$), 5.8—6.0 (2H, m, $C\underline{H}=C\underline{H}$), 7.2—7.6 (5H, m, Ph). MS *m/z*: 203 (M$^+$ − 15), 121 (100%).

2-Cyclopentene (6)——(a) From **5a**: A mixture of 4-butoxy-2-cyclopentenol$^{5)}$ (**5a**) (10.0 g, 64.0 mmol) containing *p*-toluenesulfonic acid monohydrate (120 mg, 0.64 mmol) was gradually heated to 105 °C under reduced pressure (20 mmHg) in a distillation flask with stirring. The distillate containing 2-cyclopentenone (**6**) and *tert*-butyl alcohol (discernible by ^{1}H-NMR) was collected in a cold trap immersed in liquid nitrogen, then taken up into methylene chloride (50 ml). This solution was dried over anhydrous magnesium sulfate. After evaporation of the solvent at atmospheric pressure, the temperature was raised in order to distill 2-cyclopentenone (**6**) (3.07 g, 58.5%) as a colorless oil: bp 154—156 °C (lit.$^{1)}$ bp 151—154 °C).

(b) From **5b**: A mixture of 4-cumyloxy-2-cyclopentenol (**5b**) (13.95 g, 64.0 mmol) and *p*-toluenesulfonic acid monohydrate (120 mg, 0.64 mmol) was treated as described for **5a**. The distillate containing 2-cyclopentenone (**6**) and isopropenylbenzene (discernible by ^{1}H-NMR) was chromatographed on a silica gel column (SiO$_2$, 50 g) with *n*-hexane (to elute isopropenylbenzene) followed by methylene chloride as eluants. The methylene chloride eluate was distilled at atmospheric pressure to give 2-cyclopentenone (**6**) (4.02 g, 76.6%) as a colorless oil.

References and Notes

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7) Cumyl hydroperoxide was purchased from Merck and was used without purification.