Robinson Annelation by Reactions of 2-Methyl 1,3 Diketones with a β-Chloro Ketone

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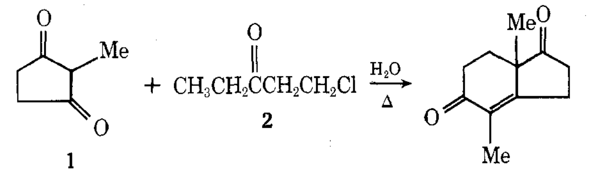
Recently we reported that octalones could be obtained by reaction of a β-chloro ketone[2] with 2-methylcyclohexanone in the presence of an acid in benzene. We now report that a Robinson annelation reaction can be achieved by reaction of 2-methylcyclopentane-1,3-dione (**1**) with 1-chloro-3-pentanone (**2**) in water to afford good yields of 7,7a-dihydro-4,7a-dimethyl-1,5(6*H*)-indandione[3] (**3**). In this method the 1,3 diketone serves as an acid catalyst in the in situ generation of the vinyl ketone, and the generated HCl acts as a catalyst in both the Michael and aldol steps of the reaction.



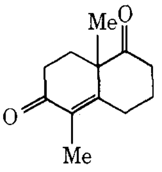
1 **2** **3**

The results of the synthesis of 7,7a-dihydro-4,7a-dimethyl-1,5(6*H*)-indandione (**3**) using different molar ratios of **1** and **2** are summarized in Table I. As shown in Table I, the yields of **3** range from 73 to 78%.

Table I. Indandione Formation Using Different Molar Ratios

Molar ratio 1:2	% yield of 3	
	Distilled	Chromatographed
1:1	72.6	62.2
1:1.5	78.1	68

Although the indandione **3** was obtained in good yield as described above, an identical reaction employing 2-methylcyclohexane-1,3-dione and 1-chloro-3-pentanone afforded after column chromatography only 23% of 5,8a-dimethyl-3,4,8,8a-tetrahydro-1,6(2*H*,7*H*)-naphthalenedione[4,5] (**4**), the major compound being the keto acid[5,6] **5** (41% yield), mp 58–61 °C (known mp 59–61 °C). The keto acid **5** presumably results from opening of the bridged[7] aldol intermediate **6** followed by dehydration of the resulting β-hydroxy ketone.



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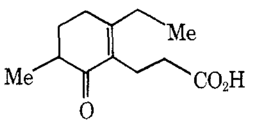

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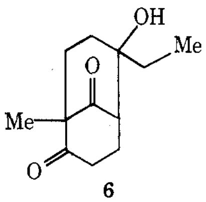

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Experimental Section

7,7a-Dihydro-4,7a-dimethyl-1,5(6*H*)-indandione (3). 2-Methylcyclopentane-1,3-dione (2.5 g, 0.022 mol) and 1-chloro-3-pentanone (4.0 g, 0.033 mol) were added to 20 ml of H_2O. The mixture was stirred at room temperature for 4 h and then refluxed for 16 h. The reaction mixture was poured into a 10% $NaHCO_3$ solution (50 ml); water (100 ml) was added and the resulting mixture was extracted with two 100-ml portions of chloroform. The chloroform extracts were washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated on a rotary evaporator. Distillation of the residue gave 3.1 g (78.1%) of 7,7a-dihydro-4,7a-dimethyl-1,5(6*H*)-indandione (**3**), bp 94–98 °C (0.01 mm). Chromatography of the oil (3.1 g) on silica gel and elution with ether–hexane afforded 2.7 g (68%) of pure **3**: NMR (CCl_4) δ 1.30 (s, angular methyl, 3 H), 1.73 (s, 3 H), 1.78–3.09 (methylenes, 8 H); ir (neat) 1660 and 1745 cm $^{-1}$.

Registry No.—**1**, 765-69-5; **2**, 32830-97-0; **3**, 28255-09-6; **4**, 28255-08-5; **5**, 60065-15-8; **6**, 60065-16-9; 2-methylcyclohexane-1,3-dione, 1193-55-1.

References and Notes

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(6) We would like to thank Professor A. Yoshikoshi for kindly providing us with the NMR, ir, and an authentic sample of the keto acid **5**.
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Air Oxidation of Cyclopentadecane

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The oxidation of hydrocarbons has been thoroughly studied[1–4] and it has been found that the hydroperoxide initially formed decomposes mainly by a nonchain process to yield the alcohol plus ketone.[5] It has been suggested that the alcohol is the initial product, and the ketone is formed by further oxidation. As the reaction proceeds, the alcohol and ketone are consumed with the formation of by-products (eq 1).

$$RH \xrightarrow{O_2} ROOH \rightarrow ROH \rightarrow \text{ketone} \rightarrow \text{by-products} \qquad (1)$$

The selectivity of the oxidation of hydrocarbons to alcohol can be improved by the addition of boric acid[6] to the oxidation mixture. This increased selectivity was initially believed to be due to the formation of borate esters of the alcohols which retarded the oxidation of the alcohol and subsequent by-product formation.[4]

It has been proposed, however, that the function of boric acid (metaboric acid) is not solely to esterify the alcohols to protect them against oxidation, but to catalyze the decomposition of the hydroperoxides.[7–9] Indeed, it has been shown that the boric acid esters are as effective as boric acid itself in directing the oxidation of paraffins to alcohols in concentrations as low as 0.2% ester.[10]

In this note, we report our observations on the air oxidation of cyclopentadecane. The products are important precursors in musk synthesis.[11]

Results and Discussion

The results of some experiments on the air oxidation of cyclopentadecane are shown in Table I. The yields of alcohol and ketone from this cyclic hydrocarbon compare well with the yields of alcohol and ketone from the air oxidation of cyclododecane.[12] The results confirm previous observations that product yields and conversions in air oxidations are dependent on air flow rate, boric acid, and temperature among other variables.[4]

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