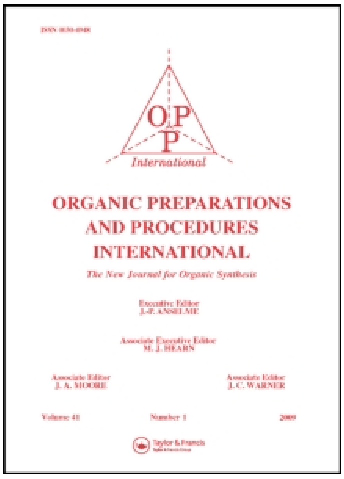

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CHROMIC ACID OXIDATION OF INDANS AND HYDRINDACENES. SYNTHESIS OF 1,1-DIMETHYLINDENE

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CHROMIC ACID OXIDATION OF INDANS AND HYDRINDACENES. SYNTHESIS OF 1,1-DIMETHYLINDENE

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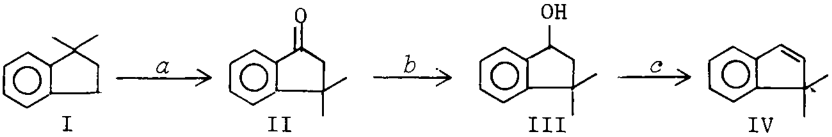
The oxidation of indans and hydrindacenes is an attractive synthesis step since the resulting ketones are useful intermediates for preparing indenes and their homologs by reduction[2] and dehydration.[3] The conversion to ketones also may be used for purification of indans and hydrindacenes since they and their derivatives are readily reconverted to hydrocarbons by hydrogenolysis.[4]

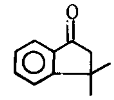
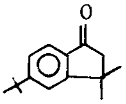
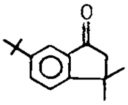
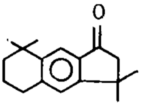
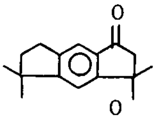
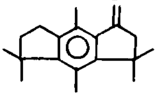
Acid-catalyzed cyclialkylation of arenes[5a-d] has made a broad variety of indans and hydrindacenes available for study. We have used chromic anhydride-acetic acid oxidation to obtain 3,3-dimethyl-1-indanone (II) and the other ketones listed in Table I. In addition, we have reduced and dehydrated II to 1,1-dimethylindene (IV) in 67% overall yield as shown.



$^{a}CrO_3$, CH_3CO_2H. $^{b}(C_4H_9)_2AlH$. ^{c}Amberlyst 15 in cyclohexane, Δ.

The most effective method for carrying out the oxidation step of the sequence involves the use of an excess of a stirred *dilute* solution of CrO_3 in acetic acid at room temperature. This simple procedure affords the yields of ketones shown in Table I. Our earlier efforts to perform this oxidation in more concentrated solution[6a] or in acetic anhydride[6b] gave low yields owing to incomplete or excessive oxidation. The use of silver

TABLE I
CHROMIC ANHYDRIDE OXIDATION PRODUCTS

Ketone		m.p., °C	% Yield	% Calcd (Found)	
				C	H
II		bp 70° (0.2 mm)[a]	88		
V		49-51[b]	92		
VI		50-51[c]	87		
VII		81-82	87	84.16 (84.30)	8.83 (8.76)
VIII		98-99	90	84.16 (84.28)	8.83 (8.67)
IX		186-188	88	84.32 (84.30)	9.44 (9.44)

[a] Lit.[5d] b.p. 107° (4.7 mm). [b] Lit.[7] b.p. 180-182° (14 mm). [c] Lit.[8] 51-51.8°

persulfate[6c] gave multiple products (glc analysis), and oxidation with potassium permanganate using a phase-transfer technique[6d] was ineffective.

EXPERIMENTAL[9a,b]

General Conditions of the Reaction. A sample of the hydrocarbon (1 to 15 g.) is dissolved in 1 l. of acetic acid.[10] A 10% solution of CrO_3 (prepared by dissolving 21 g. of CrO_3 in 190 ml. of acetic acid and 10 ml. of water) is introduced to the magnetically stirred solution through an addition funnel at a rate such that the reaction temperature remains below 30°. Best results were obtained by using twice the stoiciometric amount of 4/3 moles of CrO_3 per methylene group.

The reaction mixture is stirred overnight and then diluted with six volumes of water. The mixture is extracted with ether or filtered, depending upon the physical properties of the product monoketone. The following procedures are illustrative.

Oxidation of 1,1-Dimethylindan (I) to 3,3-Dimethyl-1-indanone (II). To a stirred mixture of 5.85 g. (0.04 mole) of I dissolved in 1 l. of acetic acid was added 107 ml. of 10% CrO_3 in acetic acid (see above) over a 30-min. period. The reaction temperature remained below 30°. The solution was stirred overnight, diluted with 5 l. of water, and extracted with two 1-l. portions of ether. The combined ether extract was washed with 10% NaOH, dried ($MgSO_4$), and concentrated by distillation. This procedure gave 6.0 g. of orange-colored oil. Distillation gave 5.6 g. (88%) of colorless II: ir (film) 1709 (C=O) cm^{-1}; nmr (CCl_4) δ 7.59-7.05 (m, 4, ArH), 2.44 (s, 2, $ArCOCH_2$), and 1.40 (s, 6, *gem*-CH_3); glc[9a,b] single peak.

3,3-Dimethyl-1-indanol (III). To a 3-necked, 2-l. flask equipped with Teflon-coated magnetic stirring bar, nitrogen flush, and a thermometer was added 400 ml. of dry benzene and 29 g. (0.2 mole) of diisobutylaluminum hydride.[2] The flask was immersed in cold water and a solution of 24 g. (0.15 mole) of crude 3,3-dimethyl-1-indanone in 400 ml. of benzene was added over 20 min. Stirring was continued for an additional 20 min. and then the reaction mixture was poured onto ice. The pH of the mixture was adjusted to *ca*. 4 with 15% HCl. The mixture was extracted with three 600-ml. portions of ether, and the combined ether extract was washed with 10% NaOH and dried ($MgSO_4$). Evaporation left 24 g. of yellow oil. Distillation gave 22.5 g. (94%) of III: bp. 71° (0.2 mm) [lit.[5d] 107° (4.2 mm)]; ir (film) 3360 (OH) cm^{-1}; the nmr spectrum agreed with lit.[5d] values; glc[9a,b] single peak.

1,1-Dimethylindene (IV). To a 1-l., 2-necked flask equipped with stirring bar, addition funnel, and Dean-Stark trap were added 10 g. of dried Amberlyst-15[13] and 300 ml. of dry cyclohexane. The stirred mixture was brought to reflux. A 24-g. (0.15 mole) sample of 3,3-dimethyl-1-indanol was added over a 20-min. period. Reflux was continued for 30 min., the mixture was filtered, and cyclohexane was distilled from the filtrate to give 21 g. of oil. Distillation gave 17.3 g. (81%) of IV: bp. 33° (0.2 mm) (lit.[5d] 57° (4.8 mm)]; the nmr spectrum agreed with the published spectrum;[5d] glc[9a,b] single peak.

An oxidation and isolation procedure identical to that described for the conversion of I to II gave:

5-*tert*-Butyl-3,3-dimethyl-1-indanone (V): ir (film) 1712 (C=O) cm^{-1}; nmr (CCl_4) δ 7.38, 7.31 (s, 2, ArH), 2.42 (s, 2, $ArCOCH_2$), 1.40 (s, 6, *gem*-CH_3), and 1.35 (s, 9, $C(CH_3)_3$); glc[9a,b] single peak.

6-*tert*-Butyl-3,3-dimethyl-1-indanone (VI): ir (film) 1720 (C=O) cm^{-1}; nmr (CCl_4) δ 7.48 (m, 2, ArH), 7.30 (s, 1, ArH), 2.43 (s, 2, $ArCOCH_2$), 1.39 (s, 6, *gem*-CH_3), and 1.33 (s, 9, $C(CH_3)_3$); glc[9a,b] single peak.

3,3,7,7-Tetramethyl-*s*-hydrindacen-1-one (VII). A mixture of 4 g. (0.18 mole) of 1,1,5,5-tetramethyl-*s*-hydrindacene,[5b] 1 l. of acetic acid[10] and 50 ml. of 10% CrO_3 in acetic acid (see above) was prepared and stirred for 24 hr. Water (6 l.) was added and the pink slurry was filtered.

The filtrate was extracted with three 1-l. portions of ether; the ether solution, after drying ($MgSO_4$) and evaporation, gave 1.17 g. of orange solid. This was combined with the solid isolated by filtration and the mixed crystals were recrystallized from petroleum ether (bp. 68°) and sublimed at 75° (0.1 mm) to give 3.7 g. (87%) of colorless VII: ir (KBr) 1715 (C=O) cm^{-1}; nmr (CCl_4) δ 7.28, 7.13 (s, 2, ArH), 2.92 (t, 2, $ArCH_2$), 2.43 (s, 2, $ArCOCH_2$), 1.95 (t, 2, $ArCH_2C\underline{H}_2$) and 1.38, 1.28 (s, 12 *gem*-CH_3); glc[9a,b] single peak.

A procedure similar to that used for preparation of VII was used to prepare VIII and IX.

3,3,5,5-Tetramethyl-*s*-hydrindacen-1-one (VIII): ir (KBr) 1705 (C=O) cm^{-1}; nmr (CCl_4) δ 7.39, 7.09 (s, 2, ArH), 2.93 (t, 2, $ArCH_2$), 2.47 (s, 2, $ArCOCH_2$), 1.97 (t, 2, $ArCH_2\underline{CH}_2$ and 1.42, 1.30 (s, 12, *gem*-CH_3); glc[9a,b] single peak.

3,3,4,5,5,8-Hexamethyl-*s*-hydrindacen-1-one (IX): ir (KBr) 1710 (C=O) cm^{-1}; nmr δ 2.73 (t, 2, $ArCH_2$), 2.43 (overlapping s, 5, $ArCH_3$ and $ArCOCH_2$), 1.89 (t, 2, $ArCH_2\underline{CH}_2$) and 1.49, 1.36 (s, 12, *gem*-CH_3).

The ketone IX was prepared from previously undescribed 1,1,4,7,7,8-hexamethylhydrindacene:[5a] mp. 135-136°; nmr (CCl_4) δ 2.62 (t, 4, $ArCH_2$), 2.28, 2.03 (s, 6, $ArCH_3$), 1.82 (t, 4, $ArCH_2\underline{CH}_2$), 1.31 (s, 12, *gem*-CH_3).

Anal. Calcd. for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 89.29; H, 10.76.

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(1) (a) American Petroleum Institute, Graduate Research Assistant, 1968-1972.
(b) Address reprint requests to this author.

(2) Literature and a sample of diisobutylaluminum hydride were kindly supplied by T. F. Davenport, Jr., Commercial Development Department, Ethyl Corp., Baton Rouge, La.

(3) Literature and a sample of Amberlyst-15 sulfonic acid resin were donated by Rohm and Haas Co., Independence Mall West, Philadelphia, Pa.

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(9) (a) Glc analysis at 229° on a 11-ft x 0.25-in. column packed with acid-washed, 80-100 mesh Chromosorb G coated with 5% UC W-98 silicone rubber showed 2.1, 2.3, 3.4, 3.7, 7.3, 7.3, 10.8, 10.8, and 21.8 min. retention times for IV, I, III, II, V, VI, VII, VIII, and IX respectively.
(b) Glc analyses at 235° on a 5-ft. x 0.25-in. column packed with 30-60 mesh, acid-washed Gas Pack W coated with 25% Carbowax 20M showed 1.6, 1.7, 5.4, 6.3, 9.2, 10.2, 16.0, 18.4, and 37.5 min. retention times for I, IV, II, III, V, VI, VII, VIII, and IX respectively. The glc analyses were made on a Hewlett-Packard 5750 instrument.

(10) Oxidation of I as described (0.04 mole of I/1. of acetic acid) gave a complete reaction. When a concentration of 0.14 mole of I/1. was used, 25% of I remained unreacted.

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