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Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. VII. Reaction of 5-Indanol with Methanol[1a]

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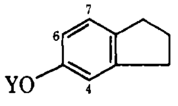
The alumina-catalyzed reaction of 5-indanol (1) with excess methanol was investigated as a function of temperature (330–520°) and catalyst acidity. 4,5,6,7-Tetramethylindan (3), 4,5,6,7-tetramethylindene (4), and 2,4,5,6,7-pentamethylindene (5) are the major products formed at 390–520° over a catalyst (B) containing sodium ion. Compound 4 is the main component (37–50 mol % yield, based on converted 1) at 390–420°, whereas 3 is favored (44–54 mol %) at 470–520°. At 470°, methanol serves as a hydrogen donor (for the forward reaction) in the quasi-equilibrium system $4 + 2\text{H} \rightleftharpoons 3$. With a sodium-free catalyst (A), 3 is the main product from 1 at 390–420° (61 mol %), whereas 4 is a minor component. With A, the yield of 5 decreases (from 27 to 13 mol %) with increasing temperature in the range of 330–390°. Compound 5 was also synthesized by a noncatalytic method.

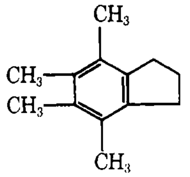
It was shown previously[2-4] that phenol and naphthols react with methanol at 400–550° in the presence of alumina catalysts to form polymethylarenes. At milder temperatures the formation of oxygen-containing intermediates, *i.e.*, methylated hydroxyarenes and hydroaromatic ketones, was observed. As an extension of these studies the alumina-catalyzed reaction of 5-indanol (1) with methanol, and its dependence on temperature (330–520°) and catalyst acidity, was investigated. Since 1 is a substituted phenol, facile methylation of the aromatic ring was anticipated above 300°.

The experimental and analytical procedures were similar to those employed previously.[2-4] Catalysts used were A (sodium free alumina, obtained by hydrolysis of aluminum isopropoxide) and B (Harshaw alumina containing *ca.* 0.4% of sodium ion).[5] The molar ratio of methanol to 1 was 20:1 in all runs. Experimental data are summarized in Tables I and II.

As noted in Table I, there are three main products formed by reaction of 1 with methanol at 390-520° in the presence of B, or at 330-470° in the presence of A, *viz.*, 4,5,6,7-tetramethylindan (3), 4,5,6,7-tetramethylindene (4), and 2,4,5,6,7-pentamethylindene (5). In addition, 5-methoxyindan (2) is produced with B below 400° and the yield of 2 increases as the temperature decreases toward 355°. The relative yields of 3 and 4 vary to a considerable extent with temperature and with catalyst acidity. With B, formation of 3 increases monotonously with increase of temperature from 355° (2 mol %) to 520° (54 mol %), whereas the yield of 4 reaches a maximum (*ca.* 50 mol %) near 420°. The yield of 4 is higher than that of 3 at 355-420°, while 3 is the major product at 470-520°. With A, on the other hand, 3 is the predominant component at all temperatures studied, while 4 is formed as a minor component only (expt 8-12). The maximum yield of 3 obtained with catalyst A is *ca.* 61 mol % at 420° (expt 11). Increase of temperature to 470° (expt 12) causes considerable decrease in the yield of 3, as a result of fragmentation reactions which lead to products of low molecular weight. With catalyst B the yield of pentamethylindene 5 reaches a maximum at *ca.* 390° (21 mol %, based on converted 1) and then remains nearly constant (at 9-13 mol %) in the range of 405-520°. With A the formation of 5 decreases with increasing temperature in the range of 330-420° (expt 8-11) and is 27 mol % (based on converted 1) at 330°. Altogether, for B at temperatures above 390° and for A at temperatures above 330° the average number of methyl groups per indene or indan ring present in the total identified product is close to 4.2.



1, Y = H
2, Y = CH_3



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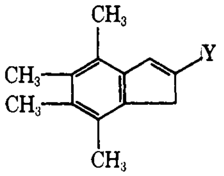


4, Y = H
5, Y = CH_3

Table II and Figure 1 show the results of a series of experiments in which a product mixture (from expt 13) was recycled five times (expt 14-18) through catalyst B at a constant temperature of 470°. A fresh portion of methanol was added to the recycled material in each run. The data show that the concentration of 3 increases with increasing reaction time and ultimately reaches a constant value of *ca.* 69 mol %, while the concentration of 4 consistently decreases to *ca.* 9 mol % (*i.e.*, the molar ratio of 3:4 of 7.7 is attained). Similarly, when one uses pure 3 as the starting material in recyclization experiments (expt 19-20) a molar ratio of 3:4 of 9.6 is attained. Extrapolation of these data (Figure 1, broken lines) to longer reaction times indicates that a convergent molar ratio of *ca.* 9.0 would result, corresponding to a pseudo-equilibrium relationship of 4 + 2H $\rightleftarrows$ 3, where the hydrogen is ultimately furnished by methanol. In contrast, the concentration of pentamethylindene 5 does not seem to be significantly altered by change in reaction time. A single recycle of the product mixture

Table I

Alumina-Catalyzed Reactions of 5-Indanol (1) with Methanol[a]

Experiment no.	1	2	3	4	5	6	7	8	9	10	11	12
Catalyst[b]	B	B	B	B	B	B	B	A	A	A	A	A
Reaction temp, °C	355	390	405	420	470	500	520	330	355	390	420	470
Conversion of 1, mol %	39	82	100	100	100	100	100	67	75	84	100	100
Product component,[c] mol %												
5-Methoxyindan (2)	15.8	10.2										
4,5,6,7-Tetramethylindan (3)	1.6	21.7	29.7	33.1	44.2	47.6	53.5	30.2	42.4	50.7	61.0	31.7
4,5,6,7-Tetramethylindene (4)	5.3	30.0	41.7	49.6	38.9	33.0	26.4	7.5	5.5	6.5	5.6	4.5
2,4,5,6,7-Pentamethylindene (5)	1.8	17.1	12.9	9.0	10.2	12.8	11.0	18.0	15.9	11.2	5.6	7.6
Unidentified[d]	13.9	2.9	13.6	13.0	10.6	9.1	13.0	11.6	12.5	16.5	19.4	39.8[e]
Depth of ring methylation[f]	1.5	2.9	4.1	4.1	4.1	4.1	4.1	4.3	4.2	4.2	4.1	4.2

[a] In each experiment a mixture of 6.7 g (0.05 mol) of 1, 32 g (1 mol) of methanol, and 10 ml of benzene was introduced into the reactor at a uniform rate over a period of 2 hr. [b] Forty grams of fresh catalyst was used in each experiment. [c] Calculated on the basis of 100 mol of starting 1 (including unreacted material). [d] Percentage by weight of total product; includes unidentified chromatographic peaks and nondistillable residues. [e] Mostly components of low molecular weight. [f] In average number of methyl groups per indan or indene moiety for all identified products (exclusive of recovered 1).

Table II
Alumina-Catalyzed Transformations in the Polymethylindan–Indene System with Methanol[a]

Experiment no.	13[b]	14[b]	15[b]	16[b]	17[b]	18[b]	19[c]	20[c]
Reaction time, hr[d]	0	2	4	6	8	10	6	12
Product component, mol %								
4,5,6,7-Tetramethylindan (**3**)	31.3	40.3	55.3	63.4	67.6	69.2	84.5	70.0
4,5,6,7-Tetramethylindene (**4**)	46.9	36.9	20.8	13.4	9.3	9.0	7.8	7.3
2,4,5,6,7-Pentamethylindene (**5**)	9.7	10.4	11.4	10.4	9.6	7.5		3.4
Unidentified[e]	12.1	12.4	12.5	12.8	13.5	14.3	7.7	12.3

[a] Reaction temperature, 470°; catalyst B. [b] Experiments 13–18 were run consecutively by recycling 6 g of a mixture of initial composition indicated under expt 13 (zero reaction time) with a fresh portion of methanol (32 g) and benzene (10 ml) for each run. [c] Experiments 19 and 20 were run by recycling pure **3** (0.5 g) with fresh methanol (16 g) and benzene (4 ml). [d] Cumulated reaction time. [e] See footnote *d*, Table I.

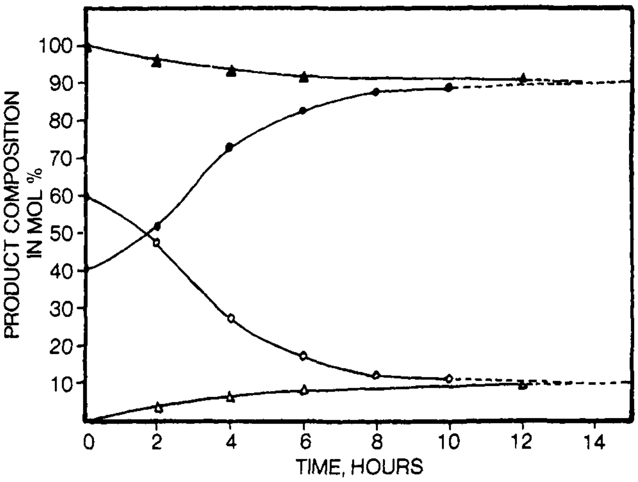
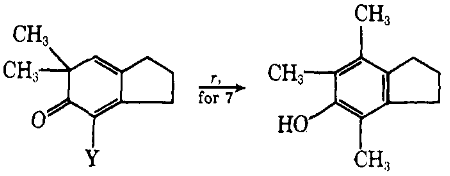


Figure 1. Interconversion of 4,5,6,7-tetramethylindan (3) and 4,5,6,7-tetramethylindene (4) at 470° in the presence of catalyst B and excess methanol, as a function of total reaction time. Starting materials: (a) a mixture (3:2, mol/mol) of 4 (open circles) and 3 (solid circles); (b) pure 3 (solid triangles), without 4 (open triangles).

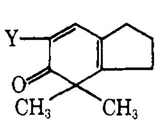
from expt 13 through B at 420° showed no appreciable interconversion of 3 and 4.

In analogy to the reactions of phenol and naphthols[2-4] with methanol in the presence of alumina, it is presumed that production of hydrocarbons 3-5 is preceded by the formation of C-methylated oxygen-bearing precursors. No attempt was made to isolate these intermediates in the indanol system. However, it seems likely that direct C-methylation of the aromatic ring in 1 will occur by electrophilic attack at C-4 and C-6 only, while methylation at C-5 and C-7 results from migration of ortho methyl substituents in the manner proposed earlier. Thus, in the previously presented shorthand notation for possible sequential pathways in the 1-naphthol series,[2c] one can derive 3 from 1 by any of the following alternative routes (listed in order of increasing energy of an intermediate): (6,4,6),*r*,6,*Rr*, (6,4,6),*r*,4,*Rr*, 6,6,*r*,4,4,*Rr*, 7a,*r*,(6,4,6),*Rr*, and 7a,*r*,(6,4,4),*Rr*, where the numbers refer to successive positions of ring methylation, parenthesized numbers represent allowed permutations in the methylation sequence, *r* symbolizes the dienone-phenol rearrangement (as in the transformation 7 → 8), and *Rr* indicates the terminal reduction-rearrangement process. If dimethylation occurred at C-4 more readily than at C-6 under the conditions used, one should have found appreciable amounts of 4,5-dimethylindan and 4,5,6-trimethylindan (formed *via* intermediates **9** and **10**, respectively) among the isolable products. The difference in facility toward dimethylation at these two positions may be ascribed to the fact that each of the molecules **9** and **10** contains a high-energy eclipsed (by the hydrogen atoms at C-3) geminal dimethyl group, while the isomeric compound **6** or **7**, respectively, does not.



6, Y = H
7, Y = CH$_3$

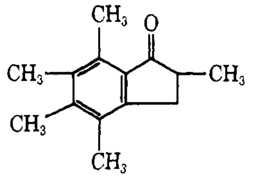
8



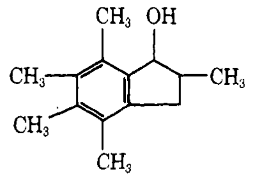
9, Y = H
10, Y = CH$_3$

Experiments 13–20 show that the rate of conversion of **3** and **4** into pentamethylindene **5** is slow in comparison to the rate of conversion of 5-indanol (**1**) into **5** (expt 5). It is suggested that in the transformation **1** → **5** dehydrogenation to an indenol plus methylation at C-2 precede the process of deoxygenation and that **8** is a likely intermediate along the reaction pathway.

The structure of **5** was confirmed by an independent synthesis starting with Friedel-Crafts alkylation of 1,2,3,4-tetramethylbenzene by means of methyl 3-bromoisobutyrate. Cyclization of the condensation product gave 2,4,5,6,7-pentamethyl-1-indanone (**11**), which was reduced to the carbinol **12** and dehydrated to **5**.



11



12

Experimental Section[6]

Procedure. Experiments 13–20 (Table II) were carried out in the apparatus described previously,[2a] while expt 1–12 (Table I) were conducted in a 60 × 2.2 cm (i.d.) stainless steel tube (isothermal zone 25 cm in length). Catalysts A and B were the same as used before and were activated at 600°.[5] In expt 1–12 the hot catalyst was washed with 10 ml of MeOH and then 100 ml of benzene after the reaction proper. Further processing was conducted as before, except that recovered acidic components were extracted into benzene and separations and identifications of reaction products were accomplished by vpc by means of a stationary phase of 10% Bentone 34 plus 5% DC-550 silicone fluid on 60–80 mesh Chromosorb W at 180°.

Isolation and Identification of Reaction Products. 5-Methoxyindan (2) [n^{25}D 1.5424; ir (CS$_2$) 1250 (Ar–O stretch) and 1070 cm^{-1} (CH$_3$–O stretch)[7]] was isolated from expt 2 and identified by *n*D and pmr.[8] 4,5,6,7-Tetramethylindan (3) [ir (CS$_2$) 2950 (s), 1380 (m), 1316 cm^{-1} (w); ir (CHCl$_3$) 1416 cm^{-1} (s)] and 4,5,6,7-tetramethylindene (4) [ir (CS$_2$) 2940 (s), 697 cm^{-1} (m, cis CH═CH); ir (CHCl$_3$) 1615 cm^{-1} (w, C═C stretch); uv max (95% EtOH) 218 nm (ϵ 17,200), 223 (16,700)] were isolated from reaction mixtures and identified by elemental analyses, as well as by comparison of melting points and pmr spectra with literature data.[9]

2,4,5,6,7-Pentamethylindene (5) was isolated from expt 3 and 8 and recrystallized from MeOH: mp 127–128° (picrate, dark red needles from EtOH, mp 145–146° dec); pmr (CCl$_4$) δ 2.08, 2.14, and 2.22 (3 overlapping s, 15, 5 CH$_3$), 3.05 (broadened s, 2, CH$_2$ at C-1), 6.52 (m, 1, H-3); pmr (CDCl$_3$) δ 2.13, 2.23, and 2.30 (3 s, 15), 3.19 (broadened s, 2), 6.60 (m, 1); ir (CS_2) 1395 (m), 905 (m), 828 cm^{-1} (m); ir ($CHCl_3$) 2950 (s), 1620 (m, C=C stretching), 1451 cm^{-1} (s); uv max (95% EtOH) 220 nm (ϵ 20,900), 225 (21,700).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.15; H, 9.82.

Isolated and synthetic samples (*vide infra*) of 5 were identical.

Syntheses of Reference Compounds. 2,4,5,6,7-Pentamethyl-1-indanone (11).[10] A mixture of 11.5 g (0.086 mol) of 1,2,3,4-tetramethylbenzene, 15 g (0.083 mol) of methyl 3-bromoisobutyrate,[11] and 50 g of anhydrous $AlCl_3$ was maintained at 135° until evolution of hydrogen halide gas ceased (2 hr). The reaction mixture was treated with ice-water and extracted with benzene. Evaporation of the extract left a solid which was recrystallized from MeOH and then stirred and heated (steam bath) with 125 ml of concentrated H_2SO_4 for 14 hr. The mixture was poured into ice-water and extracted with benzene. Evaporation gave a crude solid which was purified by repetitive evaporative distillation at 130° (0.5 mm) to give 3.7 g (22%) of **11**, mp 72–76°, converted to needles (mp 85–86°) on recrystallization from MeOH: pmr ($CDCl_3$) δ 1.31 (d, 3, J = 7.3 Hz, CH_3 at C-2), 2.64 (s, 3, CH_3 at C-7) superimposed on 1.8–3.5 (m, 12, H-2, 2 H-3, 3 CH_3);[12] ir (CS_2) 2980, 2950, 1705 (C=O),[13] 1328, 1282, 1148 cm^{-1}; ir ($CHCl_3$) 1587, 1462, 1385 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.99; H, 9.04.

2,4,5,6,7-Pentamethyl-1-indanol (12). To a stirred, cold (0°) suspension of 0.5 g of $LiAlH_4$ in 90 ml of ether was added dropwise a solution of 2 g of **11** in 10 ml of ether. After further stirring (2 hr), the cold mixture was treated with aqueous NH_4Cl and extracted with ether. Evaporation of solvent and recrystallization of the residue from MeOH gave 0.7 g (35%) of **12** as white prisms: mp 130–131°; pmr (CCl_4) δ 1.02 (d, 3, J = 7 Hz, CH_3 at C-2), 1.5–3.4 (m, 16, H-1, H-2, 2 H-3, 4 CH_3),[14] 4.6 (broad signal, 1, OH); ir (CS_2) 2970, 2940 cm^{-1}; ir ($CHCl_3$) 3625 (OH), 1464, 1387 cm^{-1}.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.03; H, 9.58.

2,4,5,6,7-Pentamethylindene (5). An intimate mixture of 0.3 g of carbinol **12** and 3 g of alumina was heated at 150° (1 atm) for 2 hr and then evaporatively distilled (150°, 0.6 mm) to give 0.14 g (51%) of crystalline **5**. Recrystallization from MeOH gave a sample which was identical with that isolated from catalytic reaction (*vide supra*).

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Registry No.—**1**, 1470-94-6; **2**, 5111-69-3; **3**, 707-95-9; **4**, 707-96-0; **5**, 50415-46-8; **5** picrate, 50415-47-9; **11**, 50415-48-0; **12**, 50415-49-1; methanol, 67-56-1; 1,2,3,4-tetramethylbenzene, 488-23-3; methyl 3-bromoisobutyrate, 20609-71-6.

References and Notes

(1) (a) This investigation was supported by Research Grant No. CA-5969 from the National Cancer Institute, U. S. Public Health Service. (b) NATO Postdoctoral Fellow, 1966–1967. (c) On leave from the Department of Chemistry, Weizmann Institute of Science, Rehovoth, Israel, 1964–1969.

(2) (a) L. H. Klemm, J. Shabtai, and D. R. Taylor, *J. Org. Chem.*, **33**, 1480 (1968); (b) *ibid.*, **33**, 1489 (1968); (c) *ibid.*, **33**, 1494 (1968); (d) *ibid.*, **35**, 1075 (1970).

(3) L. H. Klemm, J. Shabtai, and C. E. Klopfenstein, *J. Org. Chem.*, **35**, 1069 (1970).

(4) L. H. Klemm and D. R. Taylor, *J. Org. Chem.*, **35**, 3216 (1970).

(5) For simplicity, catalysts are designated by the same capital letters, respectively, as used in earlier papers.[2,3] For determination of acidities of these catalysts see ref 2a and papers cited therein.

(6) Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were obtained by means of a Beckman IR-7 spectrometer; pmr spectra by means of a Varian Associates A-60 instrument, with tetramethylsilane as internal reference; and ultraviolet spectra by means of a Cary 15 spectrophotometer.

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(10) This synthesis followed a general procedure given in ref 9.

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(12) The methyl signals occur as overlapping singlets in the region δ 2.2–2.3.

(13) *Cf.* values of 1705–1710 cm^{-1} for indanone and methyl-substituted indanones: "Sadtler Standard Infrared Spectra Catalog," Spectra No. 3426, 4890, 14324.

(14) The methyl signals occur as overlapping singlets in the region δ 2.1–2.3.

Noble Metal Catalysis. III. Preparation of Dialkyl Oxalates by Oxidative Carbonylation

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Dialkyl oxalates can be prepared in good yields by oxidative carbonylation in the presence of alcohols and dehydrating agents using a palladium redox system and oxygen. The other product, water, is removed by the dehydrating agent. If the dehydrating agent is not effective, then large amounts of carbon dioxide are made and no oxalates are found. At low carbon monoxide pressure increased amounts of dialkyl carbonate are also found. Of the various cocatalysts tried, a cupric chloride–cuprous chloride system was found to be the most selective.

Dialkyl oxalates can be prepared in good yields by oxidative carbonylation[1] in the presence of alcohol and dehydrating agents using a palladium redox system according to eq 1 and 2.

$$2CO + 2ROH + \tfrac{1}{2}O_2 \longrightarrow RO_2CCO_2R + H_2O \qquad (1)$$

$$H_2O + (RO)_3CH \longrightarrow 2ROH + HCO_2R \qquad (2)$$

The dehydrating agent is necessary; otherwise large amounts of carbon dioxide are produced and no oxalates are found. The palladium redox system is somewhat similar to the one used in acetaldehyde synthesis,[2] but optimum results are achieved by restricting the amounts of chloride ion. In addition, carbonates are produced by much the same chemistry.

Results

The major products of the reaction are oxalates and carbonates, but, in addition, there are also produced under some conditions significant amounts of carbon dioxide and esters arising from solvent attack. Under acidic conditions some alkyl halides and ethers are also produced. Table I shows some of the results concerning the synthesis of diethyl oxalate using two of the three useful cocatalysts, iron and copper halides. An example of the third cocatalyst type, the quinones, is shown in the Experimental Section.

A comparison of runs 1 and 3 shows that although ferric chloride gives much the better ratio of oxalate to carbonate than does cupric chloride, ferric chloride causes the