# Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. IV. Products and Mechanism of Reaction of 2-Naphthol with Methanol[1]

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*Received March 17, 1969*

The alumina-catalyzed reaction of 2-naphthol (**2**) with excess methanol was studied as a function of catalyst acidity and temperature (275–470°). At 350–470° **2** undergoes mainly (45–96 mol % on converted naphthol) ring methylation with concurrent elimination of the arenolic group to give the following specifically substituted naphthalenes as principal products: 1,2-dimethyl-, 1,2,3-trimethyl-, 1,2,3,4-tetramethyl-, and 1,2,3,4,6-pentamethylnaphthalene. Yields of 1,2,4-trimethyl- and 1,2,3,4,6,7-hexamethylnaphthalene become significant at higher temperatures (420–470°), with a sodium-free catalyst (A). At 275–300°, with sodium-containing catalysts (C, D), the product consists mainly (57–75 mol % on converted **2**) of the oxygen-containing precursors 1-methyl-2-naphthol, 1,1-dimethyl-2-oxo-1,2-dihydronaphthalene (**6**), and 1,1,3-trimethyl-2-tetralone (**7**). At 275°, with C, **6** reacts with methanol to yield 1,2-dimethylnaphthalene (60%) and **7** (36%). At 300°, with A, **7** plus methanol give 1,2,3-trimethylnaphthalene in 94% yield. The preferential methylation of **2** at C-1 and the methylation of **6** at C-3, observed at 275–300°, are consistent with calculated simple Hückel molecular orbital reactivity indices for electrophilic attack on the corresponding systems. Mechanistic and stereochemical aspects of the reactions are discussed.

It was found previously[2] that the alumina-catalyzed reaction of 1-naphthol (**1**) with methanol, to form polymethylnaphthalenes containing two to six substituents, occurs with a high degree of positional selectivity. It was proposed (on the basis of quantum mechanical calculations, isolation and identification of oxygen-bearing intermediates, and observed specific structures of the final products) that ring methylation involves electrophilic attack preferentially at C-2, C-4, and C-7. Dimethylation at C-4 and C-7 is followed by rearrangement of a methyl group to C-3 and C-6, respectively, while dimethylation at C-2 is followed by reduction–rearrangement, whereby migration of a methyl group to C-1 occurs with attendant loss of the oxygen function and termination of the overall process.[3] As a continuation of this study, the reaction of 2-naphthol (**2**) with methanol was investigated. The direction of ring methylation in this case is of particular interest in view of the reported low reactivity of the C-3 position (as compared with the C-1 position) in **2** in a number of electrophilic substitutions.[4]

The apparatus and procedure were essentially the same as employed in the study of **1**.[2] Experiments were carried out at 275–470° and alumina catalysts used were A, sodium-free, prepared by hydrolysis of aluminum isopropoxide; C, Houdry hard alumina, containing *ca.* 0.4% of sodium; and D, from sodium aluminate, containing *ca.* 0.5% sodium.[2,3,5] Individual compounds were isolated from the total products by preparative gas chromatography and were identified by a combination of infrared and nmr spectral methods, and, in some cases, by conversion into derivatives. Quantitative analyses were carried out by gas chromatography.

## Results

Results obtained are summarized in Table I. As in the case of 1-naphthol,[2] the reaction of 2-naphthol with methanol yields four types of products in the temperature range studied, *i.e.*, methyl naphthyl ethers (**3**, **4**), methylated naphthols (almost entirely **5**), methylated oxo compounds (**6**, **7**), and methylnaphthalenes (**8–17**). The change in the relative yields of these types of products as a function of temperature and catalyst acidity follows a pattern similar to that observed in the reaction of 1-naphthol. Formation of ethers **3** and **4** occurs mainly at the lower temperatures (275–300°), and the relative importance of this reaction decreases with increased catalyst acidity (*cf.* expt 1–6; catalyst acidity A > C > D). The main reaction at 275–300° over the weakly acidic catalysts C and D (expt 1, 2, 4, 5) is ring methylation of **2** to give oxygen-bearing compounds **5–7** (combined yield 57–75 mol % on converted **2**). Only small amounts of methylnaphthalenes, mainly **11** and **12**, are formed in these experiments. However, the yields of **11** and **12** plus **14** and other polymethylnaphthalenes are markedly higher with the strongly acidic catalyst A (expt 3, 6). The combined yield of the oxygen-bearing compounds **5–7** with catalyst C or D passes through a maximum at *ca.* 300°. There is a gradual decrease in the yield of these components and a concomitant increase in the yield of methylnaphthalenes as the temperature is raised. These trends are consistent with the previously established role of methylated naphthols and oxo compounds as intermediates in the formation of methylnaphthalenes from 1-naphthol.[2,3,6] More facile conversion of the intermediate compounds occurs with catalyst A than with catalyst C or D. It is found that the combined yields of methylnaphthalenes from 2-naphthol with A at 275° (33 mol %) and at 300° (51 mol %) are considerably higher than those from 1-naphthol under identical conditions (13 and 28 mol %, respectively).

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[1] This investigation was carried out in the Department of Chemistry, University of Oregon, and was supported by Research Grants CA-5969 from the National Cancer Institute and GM 12730 from the National Institute of General Medical Sciences, U. S. Public Health Service.

[2] Part I: L. H. Klemm, J. Shabtai, and D. R. Taylor, *J. Org. Chem.*, **33**, 1480 (1968).

[3] Part II: J. Shabtai, L. H. Klemm, and D. R. Taylor, *ibid.*, **33**, 1489 (1968). Note that catalyst D was from potassium aluminate (instead of from sodium aluminate) in this earlier study.

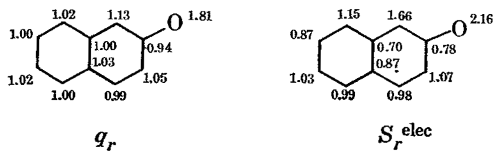
[4] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, pp 880–883.

[5] H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, **82**, 2471 (1960).

[6] Part III: J. Shabtai, L. H. Klemm, and D. R. Taylor, *J. Org. Chem.*, **33**, 1494 (1968).

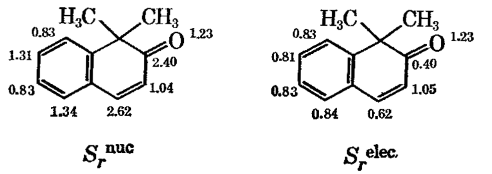
### CHART I

### MOLECULAR DIAGRAMS OF 2-NAPHTHOXY ANION. $\pi$-ELECTRON DENSITIES ($q_r$) AND SUPERDELOCALIZABILITIES FOR ELECTROPHILIC ATTACK ($S_r^{elec}$, IN UNITS OF $\beta_0^{-1}$)



### CHART II

### SUPERDELOCALIZABILITIES FOR NUCLEOPHILIC ATTACK ($S_r^{nuc}$) AND FOR ELECTROPHILIC ATTACK ($S_r^{elec}$) IN 6 (IN UNITS OF $\beta_0^{-1}$)



### TABLE I

### ALUMINA-CATALYZED REACTIONS OF 2-NAPHTHOL (2) WITH METHANOL[a]

| Expt. no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Catalyst | D | C | A | D | C | A | D | C | A | D | C | A | D | C | A |
| Reaction temp, °C | 275 | 275 | 275 | 300 | 300 | 300 | 350 | 350 | 350 | 420 | 420 | 420 | 470 | 470 | 470 |
| Conversion of 2, mol % | 38 | 40 | 71 | 51 | 52 | 78 | 84 | 87 | 92 | 89 | 95 | 100 | 93 | 100 | 100 |
| Product component,[b] mol % | | | | | | | | | | | | | | | |
| 2-Methoxynaphthalene (3) | 10.8 | 4.9 | 0.5 | 10.3 | 4.5 | 0.3 | 5.3 | Trace | ... | 0.9 | Trace | ... | ... | ... | ... |
| 1-Methyl-2-methoxynaphthalene (4) | 2.0 | 1.2 | Trace | 3.4 | 1.2 | Trace | 2.8 | Trace | ... | 0.8 | Trace | ... | ... | ... | ... |
| 1-Methyl-2-naphthol (5) | 19.3 | 26.0 | 28.5 | 25.3 | 32.3 | 19.0 | 15.0 | 13.2 | 7.5 | 6.5 | 1.2 | ... | ... | ... | ... |
| 1,1-Dimethyl-2-oxo-1,2-dihydronaphthalene (6) | 2.1 | 3.0 | 1.3 | 2.6 | 2.5 | 0.6 | 5.2 | 0.5 | <0.1 | 0.9 | 0.4 | ... | ... | ... | ... |
| 1,1,3-Trimethyl-2-tetralone (7) | 0.4 | 0.9 | 1.7 | 1.3 | 2.0 | 1.1 | 2.9 | 0.9 | <0.1 | 1.1 | 0.5 | ... | ... | ... | ... |
| Naphthalene (8) | ... | ... | ... | 0.5 | 0.6 | Trace | 2.0 | 1.8 | Trace | 6.3 | 3.8 | Trace | 2.5 | 3.4 | Trace |
| 1-Methylnaphthalene (9)[c] | ... | ... | ... | 0.2 | 0.4 | 1.4 | 2.6 | 3.5 | 2.3 | 3.8 | 4.8 | 2.6 | 3.5 | 6.4 | 1.5 |
| 1,2-Dimethylnaphthalene (11) | 1.3 | 1.4 | 12.5 | 4.2 | 4.5 | 16.3 | 20.2 | 21.5 | 17.5 | 19.0 | 22.7 | 18.0 | 19.7 | 21.9 | 13.8 |
| 1,2,3-Trimethylnaphthalene (12) | 0.2 | 0.3 | 15.8 | 0.3 | 0.7 | 20.8 | 11.4 | 18.3 | 30.2 | 20.6 | 29.0 | 16.1 | 25.8 | 21.4 | 10.6 |
| 1,2,4-Trimethylnaphthalene (13) | Trace | Trace | 1.5 | Trace | 0.1 | 2.7 | 2.0 | 2.6 | 6.5 | 3.2 | 5.8 | 12.0 | 6.7 | 6.0 | 15.9 |
| 1,2,3,4-Tetramethylnaphthalene (14) | ... | ... | 3.0 | ... | ... | 6.5 | 1.8 | 6.2 | 12.7 | 6.8 | 9.5 | 20.2 | 15.4 | 25.5 | 18.3 |
| 1,2,3,4,6-Pentamethylnaphthalene (15) | ... | ... | Trace | ... | ... | 2.1 | ... | 1.0 | 6.4 | 1.4 | 3.0 | 14.0 | 4.0 | 4.7 | 24.6 |
| Others[d] | ... | ... | 0.9[e] | ... | ... | 1.8[e] | ... | 0.7[e] | 4.2 | 1.7 | 1.9 | 11.3[f] | 2.0 | 5.0 | 11.6[g] |
| Unidentified[h] | (6.5) | (9.2) | (10.8) | (9.2) | (9.8) | (8.7) | (15.8) | (16.3) | (5.1) | (18.0) | (13.0) | (4.3) | (8.2) | (5.6) | (2.9) |
| Depth of ring methylation[i] | 0.8 | 0.9 | 1.9 | 1.0 | 1.2 | 2.3 | 1.8 | 2.2 | 3.0 | 2.3 | 2.7 | 3.7 | 2.9 | 3.0 | 3.9 |

[a] A mixture of 14.4 g (0.1 mol) of 2 and 32 g (1 mol) of methanol was used as starting material in each experiment. [b] Calculated on the basis of 100 mol of starting 2 (including unreacted material). [c] 2-Methylnaphthalene (10) is formed in low yield (0.1–0.2 mol %) above 350°. [d] 1,2,3,4,6,7-Hexamethylnaphthalene (16) and a component tentatively assigned the structure of 1,2,6-trimethylnaphthalene (17) on the basis of vpc behavior (see Experimental Section) and mechanistic considerations; includes also (especially at 420–470°) small amounts of two tetramethylnaphthalenes of undetermined structure. Formaldehyde was detected (by means of 2,4-dinitrophenylhydrazine) in the gaseous products for all runs at 350° and above. [e] Mainly 17; includes 0.2–0.3 mol % of a dimethylnaphthol. [f] Includes 4.2 mol % of 16. [g] Includes 5 mol % of 16. [h] Percentage by weight of total product; for experiments up to 350°, mainly unidentified chromatographic peaks in a range characteristic for dihydronaphthalenes; for experiments at 420–470°, carbon deposits and nondistillable residues. [i] In average number of methyl groups per naphthalene or hydronaphthalene moiety for all identified products (exclusive of recovered 2).

The isomeric compositions of the trimethyl- and tetramethylnaphthalene fractions derived from 2-naphthol (2) are markedly different from those observed in the reaction of 1-naphthol (1) under identical experimental conditions.[2] 1,2,3-Trimethylnaphthalene (12), a minor isomeric product from 1, is the predominant trimethylnaphthalene formed from 2 at temperatures up to 350° (82–99% of the isomeric fraction; expt 1–9). 1,2,4-Trimethylnaphthalene (13), normally a major component of the isomeric fraction from 1 at 275–350°, is formed as a minor component from 2 in the same temperature range. The relative importance of **13** increases, however, at 420–470° with catalyst A (expt 12, 15). Small amounts of a third isomer, tentatively assigned the structure of 1,2,6-trimethylnaphthalene, are also obtained with A (Table I, footnotes *d* and *e*). 1,2,3,4-Tetramethylnaphthalene (14), a relatively minor component from 1, comprises 90–99% of the isomeric fraction obtained from 2. Reaction of 2 also produces 1,2-dimethylnaphthalene (11), 1,2,3,4,6-pentamethylnaphthalene (15), and 1,2,3,4,6,7-hexamethylnaphthalene (16) as isomer-free components. 1-Methylnaphthalene is the predominant isomer in the monomethylnaphthalene fraction, in contrast to the formation of 2-methylnaphthalene as the main isomer from 1. Calculations based on the composition of the total products from 2-naphthol (Table I) show that the average depth of ring methylation (average number of methyl groups per product molecule) increases with catalyst acidity (A > C > D) and with temperature, up to 470°.

**Reactions of 1,1-Dimethyl-2-oxo-1,2-dihydronaphthalene (6) and of 1,1,3-Trimethyl-2-tetralone (7).**—A solution of 6 in methanol (1:10 by weight) was passed over catalyst C at 275° to yield a product which contained 1,2-dimethylnaphthalene (11), 60 mol %; 1,1,3-trimethyl-2-tetralone (7), 36 mol %; and 1,2,3-trimethylnaphthalene (12), 3.5 mol % (total conversion 52%). In a parallel experiment with catalyst A the conversion of 6 was 85% and the product consisted of 11, 41 mol %; 7, 6 mol %; and 12, 53 mol %. Passing a solution of 7 in methanol (1:10 by weight) over catalyst A at 300° gave isomerically pure 1,2,3-trimethylnaphthalene (12) in 94% yield.

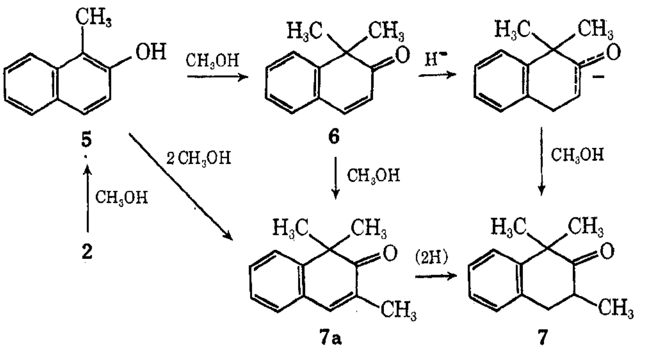
## Discussion

**Formation of Oxygen-Bearing Products.**—A qualitative indication of the expected positions for methylation in 2 was obtained by simple Hückel molecular orbital calculations of $\pi$-electron densities ($q_r$) and of superdelocalizabilities for electrophilic attack ($S_r^{elec}$) on 2-naphthoxy anion. Chart I gives the molecular diagram obtained with the set of parameters $h_{(O)} = 1.0$ and $k_{(C=O)} = 1.0$.[7] The calculated values (in particular for $S_r^{elec}$) would indicate a strong preference for electrophilic attack at the oxygen atom and at C-1. Positions C-3, C-6, and C-8 should show lower, but still significant reactivity. Although O-methylation could be favored over ring methylation, the observed relatively low yield of 2-methoxynaphthalene (Table I, expt 1–7) may be due to reversibility of the ether-forming reaction (*cf.* study of 1-methoxynaphthalene)[8] and/or to shielding of the oxygen atom by the catalyst surface.[2,8]

From the oxygen-bearing products isolated it is apparent that in the temperature range of 275–300° the first step of ring methylation occurs with a very high degree of preference at C-1, though methylation at C-3 is also significant. Thus in expt 1–5 the major product formed is 1-methyl-2-naphthol (5), while other methylnaphthols are virtually absent. Compounds **4** and **6** also result from ring methylation at C-1, while formation of 7 requires methylation both at C-1 and C-3.

Scheme I depicts likely pathways from 2-naphthol (2) to 1,1-dimethyl-2-oxo-1,2-dihydronaphthalene (6) and 1,1,3-trimethyl-2-tetralone (7) *via* 1-methyl-2-naphthol (5). Introduction of a second methyl group at C-1 would give 6, while dimethylation of 5 in the order C-1, C-3 or C-3, C-1 (*vide infra*) should form 7a. Although 7a was not isolated, its presence in the total product in concentrations below 2% is possible. Compound 7 might then result by reduction of the carbon-carbon double bond in 7a or alternatively, by initial hydride attack[10] at C-4 in 6 followed by methylation at C-3 (*vide infra* for mechanistic details).

SCHEME I



The plausibility of 6 as an intermediate on the route to 7 is provided by calculated superdelocalizabilities for electrophilic and nucleophilic attacks on the former compound (Chart II, parameters $h_{(O)} = 1.0$, $k_{(C=O)} = 1.0$).[7] If 6 is subjected to electrophilic attack by the methylating species, C-3 would be the preferred ring position for methylation. On the other hand, C-4 and (to a slightly lesser extent) C-2 would be the favored positions for hydride addition.

**Formation of Methylnaphthalenes.**—Ketones 6 and 7 (or 7a) could serve as precursors of 1,2-dimethylnaphthalene (11) and 1,2,3-trimethylnaphthalene (12), respectively. This is fully supported by the smooth conversion of 6 and 7 into the corresponding naphthalenes under the experimental conditions (*vide supra*). The facile transformation 7 → 12 is consistent with the

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[7] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, pp 123, 135. The parametric set for the 2-naphthoxy anion takes into account the expected decrease in the Coulomb integral which accompanies the increase in negative charge produced by ionization, but the molecular properties calculated from this set do not include the effects of *n* electrons on the oxygen atom.

[8] It is noteworthy that the preferential C-methylation (rather than O-methylation) of 2-naphthol, or a possible transformation 2-methoxynaphthalene → *x*-methyl-2-naphthol, is consistent with the Principle of Hard and Soft Acids and Bases (HSAB).[9]

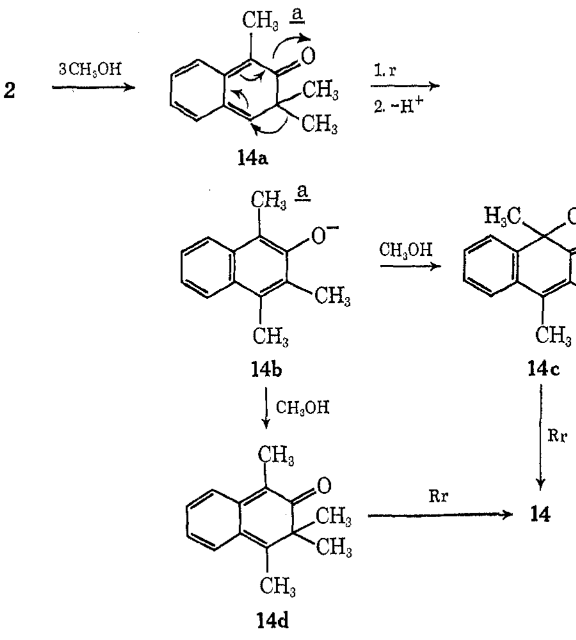
[9] R. G. Pearson, *Science*, **151**, 172 (1966); *J. Chem. Educ.*, **45**, 581, 643 (1968); R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

[10] For further discussion of the mechanism of reducing activity of the methanol–alumina system, see part V: J. Shabtai, L. H. Klemm, and D. R. Taylor, *J. Org. Chem.*, **35**, 1075 (1969).

finding[10] that, under similar conditions, 2,2-dimethyl-1-tetralone and 2,2,4,7-tetramethyl-1-tetralone are converted into 1,2-dimethylnaphthalene and 1,2,4,7-tetramethylnaphthalene, respectively. As indicated in the following paper, these reactions proceed with the intermediate formation of the corresponding 1,2-dihydronaphthalenes. The formation of **12** could similarly involve a dihydronaphthalene intermediate (*cf.* Table I, footnote *h*).

The increased yields of tri-, tetra- and pentamethylnaphthalenes above 300° indicate that ring methylation of **2** at positions other than C-1 becomes increasingly significant with rise in temperature. Whereas monomethylation at C-1 probably remains the most facile step, the introduction of a second methyl substituent at the same carbon could be preceded by methylation(s) at C-3, or both at C-3 and C-6. As in the case of 1-naphthol, it is proposed that polymethylnaphthalenes are derived from **2** by sequential pathways which involve ring methylation, dienone–arenol rearrangement (r), and a terminal reduction–rearrangement step (Rr). The formation of 1,2,3,4-tetramethylnaphthalene (**14**), for instance, is visualized as proceeding by one or more of the plausible sequences (1,3),3,r,[1,3],Rr, where the parenthesized numbers refer to allowed permutations in the methylation sequence[6] and the bracketed numbers refer to alternative positions for methylation (*cf.* Scheme II). Analogously, the sequences (1,3,6),3,r,[1,3],Rr are suggested for the formation of 1,2,3,4,6-pentamethylnaphthalene (**15**). As noted in Scheme II, dimethylation at C-3 (see **14a** and **14d**) involves the formation of a nonaromatic intermediate ketone (*cf.* Scheme II, paper III).[6] It is suggested that such highly energetic intermediates are reasonable in view of the elevated reaction temperature used and the possibility that flatwise (or nearly flatwise) adsorption of the entire π system occurs to a significant extent. Such adsorption could in fact be requisite for methylation at C-6. For a simplified picture the increased combined yield of **14** and **15** in expt 10–15 may reflect an enhancement in the reactivity of the C-3 (relative to the C-1) position in **2** with increase in temperature and catalyst acidity.

SCHEME II[a]



[a] a = acidic site.

The lack of methylation at C-8 can be attributed to *peri* interference[11] by a methyl substituent introduced at C-1 in an earlier methylation step. A similar effect was considered to prevent methylation at C-5 in 1-naphthol through earlier introduction of a methyl group at C-4.[2,6]

The small amounts of naphthalene and 1-methylnaphthalene formed in the reaction (Table I) are probably derived by direct reduction of 2-naphthol and 1-methyl-2-naphthol, respectively. 1,2,4-Trimethylnaphthalene (**13**) might be produced in a similar way from the corresponding naphthol (Scheme II, **14b**).

**Surface Ensembles and Stereochemical Mechanisms.**—The generalized mechanistic schemes which have been presented in this and preceding papers[2,3,6] stressed mainly the chemical transformations of the naphthol reactants and of reaction intermediates, with little attention paid to the nature of the methylating agent, stereochemical requirements of the catalyst surface, and the catalytic function of the alumina *per se.* It seems pertinent at this time to present a more detailed picture of the interactions between the catalyst surface and the reacting molecules. This picture is based, in part, on the model for γ-alumina developed by Peri.[12]

The catalyst surface (Figure 1a) is represented as a defect lattice work of incompletely coordinated oxide ions (strong basic sites, designated simply as "basic sites") in the outermost, partially filled surface layer, a nearly regular array of incompletely coordinated, exposed aluminum ions (designated simply as "acidic sites") in the second (filled) layer, and alternating layers of catalytically inactive oxide and aluminum ions below. The outermost layer also contains some hydroxide groups (considered weak basic sites in the fresh catalyst and amphoteric sites during the reaction proper, *vide infra*). The strength and hardness[9] of acidic sites vary over wide ranges and increase with increasing numbers of incompletely coordinated neighboring aluminum ions. For simplicity of argument, in most cases one may consider that all of the catalysts used in these studies contain only two types of Lewis acidic sites, strong and weak ones. The relative acidities of the catalysts then depend largely on the relative concentrations of these two types of sites,[5] though certain catalytic steps may occur only on the more potent of the strong sites (*i.e.*, on "very strong" sites, *vide infra*). Fully coordinated aluminum ions would not function as acidic sites. Only the outermost layer of oxide ions and hydroxide groups is considered interchangeable with the reacting species.

Based on the studies of Greenler[13] and Kagel[14] on the nature of methanol adsorbed on alumina in an equilibrated system, a detailed mechanism for formation of oxygen-bearing adsorbed intermediates is proposed (Figure 1). In Figure 1a an ensemble of four sites (two acidic, two basic) is used to illustrate initial independent processes of dissociative chemisorption of

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[11] V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).
[12] J. B. Peri, *J. Phys. Chem.*, **69**, 220 (1965); **70**, 1482, 3168 (1966).
[13] R. C. Greenler, *J. Chem. Phys.*, **37**, 2094 (1962).
[14] R. O. Kagel, *J. Phys. Chem.*, **71**, 844 (1967).

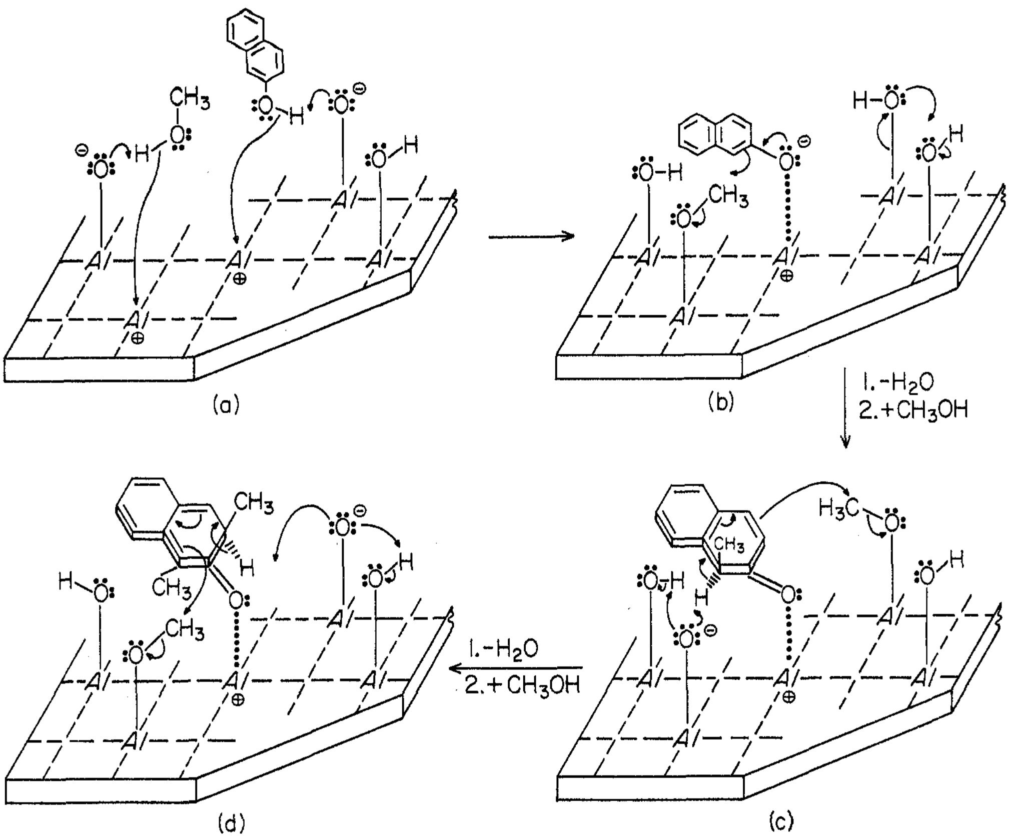

Figure 1.—Five-site ensemble for sequential methylation of **2** at C-1 and C-3.

2-naphthol[15] and methanol with formation of surface naphthoxide and methoxide[13,14,16] groups, respectively. Bonding occurs between the hard acidic site and the hard basic oxygen in both cases. However, the bonding is indicated as covalent for the methoxide and ionic (dotted line) for the naphthoxide, in accordance with the relative acidities of methanol and 2-naphthol (*i.e.*, with bonding to the proton, also a hard acid). Methylation of the adsorbed naphthoxide species at C-1 by a juxtaposed methoxide[16] is represented in Figure 1b as a concerted step, accompanied by regeneration of an oxide site (Figure 1c) at a different position on the surface. Repeated methylation of the adsorbed naphthoxide at C-1 would produce 1,1-dimethyl-2-oxo-1,2-dihydronaphthalene (**6**). On the other hand, if the second methyl substituent is introduced at C-3 (Figure 1c) and this step is followed by methylation at C-1 (Figure 1d), the product would be 1,1,3-trimethyl-2-oxo-1,2-dihydronaphthalene (**7a**, Scheme I). It is readily apparent from Figure 1 that geometric relationships of the adsorbed reactants should favor methylation at carbons vicinal to C-2, particularly if the naphthalene ring protrudes outward from the surface. At higher temperatures and/or with more acidic catalysts the ensemble of acidic sites may be more extensive in area and permit both flatwise adsorption of the naphthalene ring and access of surface methoxide groups to ring positions more distant from the oxygen function.

A fifth site (an hydroxide group) in the ensemble (Figure 1) serves to effect loss of water from the catalyst surface. This process involves proton transfer between adjacent hydroxide groups (amphoteric sites). Proton transfer may also occur from an hydroxide group to adsorbed arenoxide with the attendant loss of arenol, *e.g.*, 1-methyl-2-naphthol (**5**), from the surface. Other than in these desorption processes, however, Brönsted acidity of the catalyst surface (acquired principally during the reaction proper) is considered to be nonfunctional.[17]

A more detailed possible mechanism for the reduction–rearrangement of **6** is presented in Figures 2 and 3. In Figure 2a an ensemble of four sites (two acidic and two basic) serves to adsorb methanol and ketone **6**.[18] Adsorption is followed by hydride transfer from a methoxide group to the carbonyl function (Figure 2b) to produce formaldehyde (*cf.* Table I, footnote *d*) and a chemisorbed dihydronaphthoxide intermediate (Figure 2c). This intermediate subsequently undergoes loss of its oxygen function in the form of a surface oxide group, with concurrent neopentyl-type rearrangement of a methyl group.[10] As depicted in Figure 2c, the rearrangement involves anchimeric assistance by the migrating methyl group and $\gamma$ participation[19] by proton extraction from the other methyl group to the surface. Hydrogen exchange between the surface and the unstable intermediate **11a** (Figure 2d) should occur rapidly (with or without intervening translation of **11a** upon the catalyst surface) on an ensemble of two sites (one

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[15] This mechanism should also be applicable to the 1-naphthol system.[2]

[16] Since the system used in the present study is nonequilibrated, it is still possible that nondissociatively adsorbed methanol serves as a methylating agent; *cf.* J. R. Jain and C. N. Pillai, *Tetrahedron Lett.*, 675 (1965).

[17] H. P. Boehm, *Advan. Catal.*, **16**, 179 (1966); J. M. Parera and N. S. Figoli, *J. Catal.*, **14**, 303 (1969).

[18] In fact **6** might still be anchored to the site on which it was formed.

[19] H. Pines and J. Manassen, *Advan. Catal.*, **16**, 80 (1966); C. N. Pillai and H. Pines, *J. Amer. Chem. Soc.*, **83**, 3274 (1961). Alternatively, rearrangement could occur without $\gamma$ participation. A referee has suggested a third mechanism in which rearrangement is initiated by abstraction of the proton at C-2.

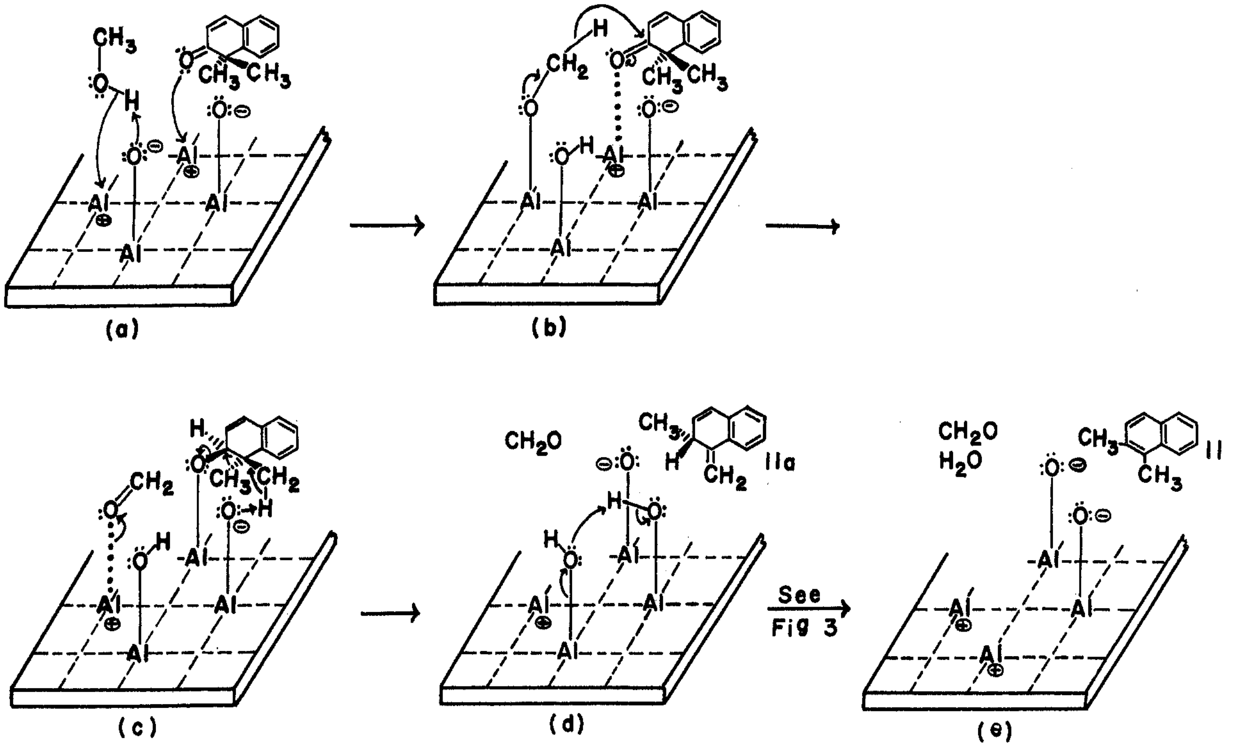

Figure 2.—Four-site ensemble for reduction–rearrangement of 6.

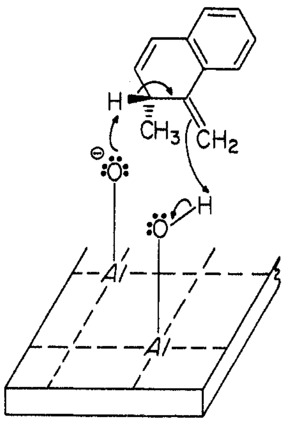

Figure 3.—Two-site ensemble for formation of 11 from 11a by hydrogen transfer.

basic and one hydroxide) to form 1,2-dimethylnaphthalene (11), as shown in Figure 3. Desorption of a molecule of water from the surface (Figure 2d), plus diffusion of water, formaldehyde, and 11 from the immediate vicinity would regenerate both ensembles of sites (but in slightly altered geometric arrangements).

## Experimental Section

**Apparatus, Catalysts, and Procedure.**—The apparatus and experimental procedure were essentially the same as employed in the study of 1-naphthol.[2] The alumina catalysts A (from aluminum isoproproxide) and D (from sodium aluminate) were prepared according to methods described previously;[2,3,5] catalyst C (Houdry Process Corp., Philadelphia, hard alumina, Grade HA 100) was obtained commercially. A fresh portion of catalyst (80 g, 0.125-in. pellets) was used in each experiment after preliminary activation *in situ* by a standard procedure.[2] In all reactions with 2-naphthol the starting mixture of reactants (Table I, footnote *a*) was passed through the reactor (total addition time, 2 hr) at a constant liquid feed rate, in a stream of nitrogen (22 ml/min), at atmospheric pressure.

**Reactions of 1,1-Dimethyl-2-oxo-1,2-dihydronaphthalene (6) and 1,1,3-Trimethyl-2-tetralone (7) in the Presence of Methanol.**—In experiments with compounds 6 and 7 the starting mixture consisted of 1 g of the ketone in 10 g of methanol. The solution was passed through the catalyst (30 g) over a period of 45 min. At the end of the run the catalyst was washed first with methanol (5 ml), then with benzene (50 ml), and finally extracted with boiling acetone. The product was processed and analyzed as usual.[2,3]

**Isolation and Identification of Reaction Products.**—The methylnaphthalenes 9–16 were identified by comparison of nmr and infrared spectra, as well as vpc retention volumes, with those of authentic samples. 1-Methyl-2-naphthol (5), mp 110–111° (lit.[20] mp 110–111°), was isolated from the acidic fractions of expt 1–6, whereas 2-methoxynaphthalene (3) and 1-methyl-2-methoxynaphthalene (4) were isolated from the neutral products of expt 1, 2, and 4. Compounds 3–5 were identified by comparison of nmr and infrared spectra (also mixture melting point for 5) with those of reference samples (*vide infra*).

1,1-Dimethyl-2-oxo-1,2-dihydronaphthalene (6) was isolated in >99% purity by preparative vpc of the products from expt 2, 4, and 7: 2,4-dinitrophenylhydrazone mp 224–225° (lit.[21] mp 224.5–225.5°); nmr ($CCl_4$) $\delta$ 1.41 (s, 6, geminal $CH_3$ groups), 6.05 (d, 1, $J$ = 10.0 Hz, =CH— at C-3), and 7.1–7.5 (m, 5, aromatic protons and —CH= at C-4); ir (neat) 764 (s), 839 (s), 1102 (m), 1216 (m), 1252 (m), 1298 (m), 1381 (w), 1399 (m), 1467 (m), 1566 (m), 1624 (w), 1670 (s), and 2990 cm$^{-1}$ (m).

In the nmr spectrum the partial overlapping of the doublet which is due to the vinylic proton at C-4 with the multiplet arising from the aromatic protons is similar to that shown by the $\beta$-vinylic and aromatic protons in the cinnamic acids.[22] The frequency of the carbonyl absorption (1670 cm$^{-1}$) falls in the range characteristic of $\alpha,\beta$-unsaturated ketones (1665–1685 cm$^{-1}$).[23a] The strong band at 839 cm$^{-1}$ is assigned to CH out-of-plane deformation at the *cis* double bond (estimated frequency, 820 cm$^{-1}$ for the *cis* CH=CH-C=O group[23b] plus 15–20 cm$^{-1}$

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[20] E. Wenkert, R. D. Youssefyeh, and R. G. Lewis, *J. Amer. Chem. Soc.*, **82**, 4675 (1960).

[21] E. N. Marvell and J. L. Stephenson, *ibid.*, **77**, 5177 (1955).

[22] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 230; E. O. Bishop and R. E. Richards, *Mol. Phys.*, **3**, 114 (1960).

[23] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1962: (a) p 132; (b) p 48; (c) p 77.

for phenyl conjugation[24]). The frequency of CH out-of-plane deformation of the four adjacent aromatic hydrogens (764 cm$^{-1}$) is close to that observed for *o*-methylstyrene (772 cm$^{-1}$).[25] The presence of geminal methyl groups is evidenced by splitting of the symmetric methyl (CH) bending vibration (doublet at 1381 and 1399 cm$^{-1}$).[26]

The nmr and infrared spectra of the product were identical with those of a sample of **6** synthesized by independent means (*vide infra*).

**1,1,3-Trimethyl-2-tetralone** (**7**) was isolated in 98% purity by vpc of the neutral products from expt 3, 5, and 7, and from a preparative experiment with compound **6** as starting material (275°, catalyst C): $n^{20}\text{D}$ 1.5440; nmr (CCl$_4$) $\delta$ 1.0–1.5 (m, 9, geminal CH$_3$ groups at C-1 and CH$_3$ at C-3), 2.4–3.2 (m, 3, CH at C-3 and CH$_2$ at C-4), and 6.9–7.5 (m, 4, aromatic protons); ir (neat) 768 (s), 1022 (m), 1054 (m), 1244 (m), 1315 (m), 1367 (w), 1386 (m), 1465 (s), 1725 (s), and 3000 cm$^{-1}$ (s).

*Anal.* Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.32; H, 8.56.

The absence of methyl substitution in the aromatic ring is evidenced by the strong band at 768 cm$^{-1}$, which is assigned to the CH out-of-plane deformation of the four adjacent aromatic hydrogens (*ortho*-disubstituted structure).[23c,25] Again the symmetric bending vibration of the geminal methyl groups is split (bands at 1367 and 1386 cm$^{-1}$). However, the doublet is rather obscured (compared with that in the spectrum of **6**), apparently as a result of overlapping with a singlet arising from symmetric deformation of the methyl group at C-3. The frequency of the carbonyl absorption (1725 cm$^{-1}$) fits the range for an unconjugated, six-membered ring ketone (1705–1725 cm$^{-1}$).

The positions of the methyl groups in **7** were confirmed by subjecting a small sample (0.8 g) to reduction with sodium borohydride, followed by dehydration of the intermediate carbinol (ir band at 3610 cm$^{-1}$) with potassium bisulfate at 2 mm pressure. The dehydration product was collected in a cold trap and aromatized by means of 2,3-dichloro-5,6-dicyanobenzoquinone[27] to give 1,2,3-trimethylnaphthalene (0.43 g, 71% overall yield), free of isomers (*cf.* analogous case for conversion of 2,2,4,7-tetramethyl-1-tetralone into 1,2,4,7-tetramethylnaphthalene).[2]

**Sources and Synthesis of Reference Compounds.**—Pure samples of the methylnaphthalenes **9**–**16** were available from previous studies.[2,8,28] 1,1-Dimethyl-2-oxo-1,2-dihydronaphthalene (**6**) was prepared according to Marvell and Stephenson;[21] 1-methyl-2-naphthol (**5**) and 1-methyl-2-methoxynaphthalene (**4**), according to Wenkert, *et al.*[20] Pure 2-methoxynaphthalene (**3**) was obtained by recrystallization of a commercial product.

**Analytical.**—Vpc analysis of neutral products was carried out on an 8 ft × 0.375 in. (o.d.) column, filled with 10% Bentone 34 (modified with 5% Apiezon L) on 60–80 Chromosorb P. The same type of column was used for the isolation of individual compounds. Most of the unidentified components (Table I, footnote *h*) showed lower retention times than methylnaphthalenes and appeared in a range characteristic for dihydronaphthalenes.[29] The analysis and isolation of acidic products was carried out on a 5 ft × 0.375 in. column filled with 10% Carbowax 20M on Chromosorb W. A Varian A-60 spectrometer was employed for the measurement of the nmr spectra, with carbon tetrachloride as a solvent and tetramethylsilane as reference compound. Infrared spectral analyses were carried out with a Beckman IR 7 spectrophotometer. The spectra of compounds **6** and **7** were measured with the pure liquids in a microcell of capillary thickness. Elemental analysis of **7** was performed by Micro-Tech Laboratories, Skokie, Ill.

**Registry No.**—**2**, 135-19-3; **6**, 23230-52-6; **7**, 23230-53-7; methanol, 67-56-1.

**Acknowledgment.**—Thanks are due to Mr. K. C. Bodily for assistance in syntheses of reference compounds.

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[24] *Cf.* 2,3-dichloro-*cis*-cinnamic acid: S. Lindenfors, *Ark. Kemi*, **13**, 127 (1959). Measurement in this laboratory shows that ethyl *cis*-cinnamate absorbs at 836 cm$^{-1}$.

[25] H. Pines and J. Shabtai, *J. Org. Chem.*, **26**, 4220 (1961).

[26] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, p 94.

[27] E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *J. Chem. Soc.*, 3123 (1960).

[28] L. H. Klemm and A. J. Kohlik, *J. Org. Chem.*, **28**, 2044 (1963).

[29] L. H. Klemm, J. Shabtai, and K. C. Bodily, unpublished results.

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# Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. V. Mechanism of Reduction of 1-Tetralones to 1,2-Dihydronaphthalenes by Means of Methanol[1a]

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*Received March 17, 1969*

The alumina-catalyzed reactions of methanol with 1-tetralone (**1**), 2,2-dimethyl-1-tetralone (**2**), and 2,2,4,7-tetramethyl-1-tetralone (**3**) were studied as a functiom of temperature (220–420°) and catalyst acidity. At 220°, with sodium-containing catalysts (C, D), **1** yields 1,2-dihydronaphthalene (**4**) as the main product (59–91 mol %, based on converted **1**). At 250–275°, with C or A (sodium-free alumina), the reduction of **1** is accompanied by methylation to give 2-methyl-3,4-dihydronaphthalene (**5**) in 75–85 mol % yield (based on converted **1**). At 325°, with A, **2** undergoes reduction–rearrangement to give 1,2-dimethyl-3,4-dihydronaphthalene (**6**) in 51 mol % yield, while at 420° the main product is 1,2-dimethylnaphthalene (80 mol %), probably derived from **6** as a precursor. The one-step conversion of 1-tetralones into 1,2-dihydronaphthalenes appears to be of general synthetic applicability. At 375–420°, with A, **3** is transformed smoothly into 1,2,4,7-tetramethylnaphthalene in 76–89 mol % yield. It is proposed that the reductive action of the alumina–methanol system involves a surface process which is mechanistically analogous to the Meerwein–Ponndorf–Verley reaction. Spectral characteristics of **4**, **5**, and **6** are reported.

It was shown previously[2] that 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene is smoothly converted into 1,2-dimethylnaphthalene (84–98% yield at 275–350°) in the presence of methanol as a reducing agent and of alumina as a catalyst. As an extension of this study, the alumina-catalyzed reactions of methanol with 1-tetralone (**1**), 2,2-dimethyl-1-tetralone (**2**), and 2,2,4,7-

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[1] (a) This investigation was carried out in the Department of Chemistry, University of Oregon, and was supported by Research Grant CA-5969, U. S. Public Health Service; (b) to whom inquiries should be addressed; (c) Research Assistant, 1964–1967.

[2] Part II: J. Shabtai, L. H. Klemm, and D. R. Taylor, *J. Org. Chem.*, **33**, 1489 (1968).