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): $n^{20}{\rm D}$ 1.5440; nmr (CCl_4) δ 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.[2,3,28] 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.

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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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).

TABLE I

ALUMINA-CATALYZED REACTIONS OF 1-TETRALONE (1) WITH METHANOL[a]

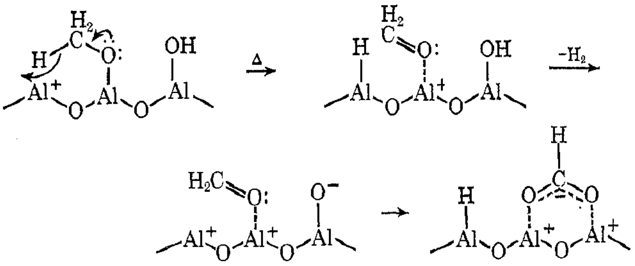
Expt no.	1	2	3	4	5	6
Catalyst	D	C	C	C	A	A
Reaction temp, °C	220	220	250	275	275	350
Conversion of **1**, mol %	48	51	74	83	97	100
Product component,[b] mol %						
1,2-Dihydronaphthalene (**4**)	43.6	30.2	17.3	15.0	14.0	21.3
2-Methyl-3,4-dihydronaphthalene (**5**)	3.9	19.8	55.5	67.5	82.0	30.5
1,2-Dimethyl-3,4-dihydronaphthalene (**6**)	...	...	...	...	<0.1	15.4
2-Methylnaphthalene (**7**)	...	...	...	<0.1	0.2	13.9
1,2-Dimethylnaphthalene (**8**)	...	...	...	...	...	10.2[c,d]

[a] The starting mixture used in each experiment consisted of 2.92 g (0.02 mol) of **1** and 32 g (1 mol) of methanol. [b] Calculated on the basis of 100 mol of starting **1** (including unreacted material). Differences between conversion and total product figures represent losses owing to unrecovered deposits on the catalyst. [c] Plus 1.9% (by weight of total product) of 1,4-dihydronaphthalene and 3.5% of unidentified products. [d] In every case the total product also included water (which formed a separate phase) and probably formaldehyde (detected by means of 2,4-dinitrophenylhydrazine solution in expt 4–6; presence not checked in expt 1–3).

tetramethyl-1-tetralone (**3**) were investigated in order to determine whether the alumina–methanol reductive system can be used for conversion of 1-tetralones into 1,2-dihydronaphthalenes (or into naphthalenes). Catalysts employed in this study were A (sodium-free alumina, obtained by hydrolysis of aluminum isopropoxide), C (Houdry hard alumina, containing *ca.* 0.4% sodium), and D (from sodium aluminate, containing *ca.* 0.5% sodium).[2-6] The acidity of these catalysts decreases in the order A > C > D, as evaluated from their activities for ring methylation of hydroxyarenes,[3-5] for dienone–arenol rearrangement of 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene,[2] and for dehydration and isomerization reactions.[6] The apparatus and procedure were similar to those used previously.[2-5] Reactions were carried out in a nitrogen atmosphere at temperatures of 220–420°. Individual compounds were isolated from product mixtures by preparative gas chromatography and identified by a combination of infrared, ultraviolet, and nmr spectral methods. The positions of methyl substituents in 1,2-dihydronaphthalene derivatives were confirmed by aromatization to the corresponding naphthalenes. Quantitative analysis of reaction products was performed by gas chromatography.

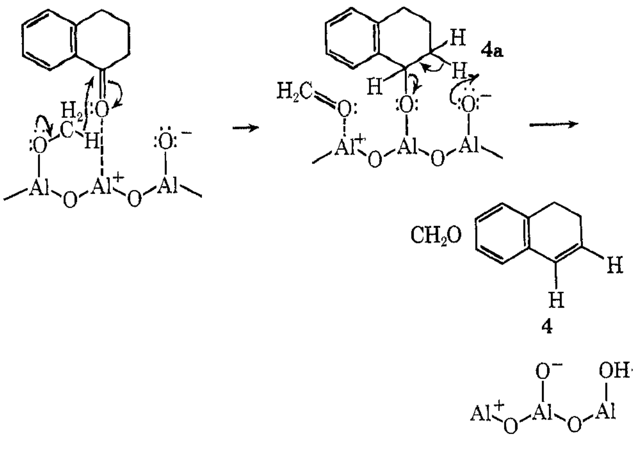
Reactions of 1-Tetralone (1).—As seen from Table I, only two products, *i.e.*, 1,2-dihydronaphthalene (**4**) and 2-methyl-3,4-dihydronaphthalene (**5**) (in addition to water and formaldehyde) are formed by reaction of **1** with methanol at 220–275° over the sodium-containing catalysts C and D. While compound **4** is a simple reduction product of **1**, formation of **5** involves methylation of **1** at C-2 as well as reduction of the carbonyl group (*vide infra*). A mechanism for the reductive action of the alumina–methanol system is suggested on the basis of infrared studies by Greenler[7] and Kagel[8] on the nature of surface species formed by methanol chemisorption on γ-alumina in the temperature range of 35–430° (in an equilibrated system). Their spectral measurements at 35–170° were consistent with the presence of surface methoxide groups, while increase in temperature above 170° caused gradual conversion of this species into a formatelike surface compound. Kagel[8] showed that this transformation is accompanied by evolution of hydrogen, which has been reported previously[9] as a major gaseous product from decomposition of methanol at 300–425° over alumina catalysts. Since formaldehyde is also produced from methanol under similar conditions,[3,5] it is likely that formation of hydrogen (from a surface methoxide) proceeds by a stepwise process, as suggested in Scheme I.[10]

SCHEME I



A possible mechanism for the formation of 1,2-dihydronaphthalene (**4**) from **1** is illustrated in Scheme II. Hydride transfer directly from a surface methoxide to the carbonyl group in **1** is assumed to produce formaldehyde and an alkoxide intermediate (**4a**). This intermediate is subsequently converted into **4** by loss of oxygen (as a surface oxide group) with concurrent elim-

SCHEME II



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

(4) Part III: J. Shabtai, L. H. Klemm, and D. R. Taylor, *ibid.*, **33**, 1494 (1968).

(5) Part IV: L. H. Klemm, C. E. Klopfenstein, and J. Shabtai, *ibid.*, **35**, 1069 (1970).

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

(7) R. C. Greenler, *J. Chem. Phys.*, **37**, 2094 (1962).

(8) R. O. Kagel, *J. Phys. Chem.*, **71**, 844 (1967).

(9) E. Briner, W. Plüss, and H. Paillard, *Helv. Chim. Acta*, **7**, 1046 (1924); K. V. Topchieva and A. P. Ballod, *Dokl. Akad. Nauk. SSSR*, **75**, 247 (1950).

(10) For simplicity, two-dimensional drawings (rather than three-dimensional ones presented previously)[5] are used in this paper.

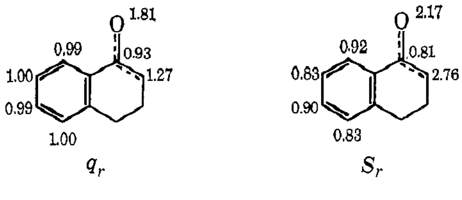
ination of a proton at C-2.[11] Alternatively, hydride transfer from a methoxide group to the carbonyl group may occur indirectly *via* a surface aluminum hydride[12–14] (*cf.* Scheme I). It seems likely that surface formate is also produced[7,8] in the reaction, though no test for its presence was made.

The mechanism in Scheme II is similar to that proposed[15] for the Meerwein–Ponndorf–Verley reduction of ketones in the presence of aluminum alkoxides (*e.g.*, ethoxide and isopropoxide).[16] Although it appears that aluminum methoxide has not been used as a reducing agent in solution, it is presumed that surface aluminum methoxide can function as such an agent under the experimental conditions employed in this study. It is observed, however, that with the alumina–methanol system the reduction product is an alkene, rather than a carbinol. Indeed, alkenes have been reported as major products of Meerwein–Ponndorf–Verley reductions in solution at elevated temperature.[16]

The formation of the other major product in expt 1–5, *i.e.*, 2-methyl-3,4-dihydronaphthalene (**5**), could involve initial removal of a proton from **1** at C-2, followed by methylation at this position, and subsequent reduction as in Scheme II. Facile methylation of 1-tetralone at the 2 position is consistent with calculated superdelocalizabilities for electrophilic attack on the anion derived from **1** (Chart I, parameters[17] $h_{(\mathrm{O})} = 1.0$, $k_{(\mathrm{C=O})} = 1.0$). The calculated S_r values for the anion indicate the possibility of more facile electrophilic attack at C-2 than at the oxygen.

CHART I

MOLECULAR DIAGRAMS OF 1-TETRALONE ANION. π-ELECTRON DENSITIES (q_r) AND SUPERDELOCALIZABILITIES FOR ELECTROPHILIC ATTACK (S_r, IN UNITS OF β_0^{-1})



The formation of 1,2-dihydronaphthalene (**4**) as the main product in expt 1 (91 mol % on converted **1**) indicates that under conditions of very low acidity (catalyst D, 220°) methylation at C-2 is negligible, whereas reduction of the carbonyl group proceeds readily. The sharply increased yield of 2-methyl-3,4-dihydronaphthalene (**5**) in expt 3 and 4, however, indicates that in the presence of moderate acidity (catalyst C, 250–275°) methylation at C-2 commonly precedes the oxygen-eliminating step (*i.e.*, reduction). Support for such a sequence was obtained in a separate experiment (with a 1:10 by weight solution of **4** in methanol as starting material) which showed that **4** is not methylated under the conditions of expt 3. The previously observed conversion[2] of 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene into 1,1,3-trimethyl-1,2-dihydronaphthalene by means of either C or D at 320° also involves ring methylation prior to oxygen elimination. The observed changes in the relative yields of **4** and **5** with a change in catalyst acidity could be explained by the effect of the acidic site on the position of bond cleavage in surface methoxide groups. For a strong acidic site the electron-withdrawing effect of the aluminum ion causes extensive polarization of the O–CH_3 bond and facilitates release of the electrophilic methylating species. For a weak acidic site, on the other hand, the polarization of the O–CH_3 bond should be relatively unimportant and ready transfer of hydride (see Scheme II) could occur in a cyclic process analogous to that envisaged in the Meerwein–Ponndorf–Verley reduction.[15] Accordingly, it is suggested that formation of **4** involves only catalysis by weak acidic sites, while that of **5** requires both weak and strong acidic sites. The relative yields of **4** and **5** would, therefore, depend on the distribution of weak and strong acidic sites in the catalysts used. Whereas weak acidic sites are present in all three catalysts, the concentration of strong acidic sites increases in the order A > C > D (where D has very few such sites, particularly at low temperature).[6]

Under conditions of both strong catalyst acidity and higher temperature (catalyst A, 350°) the reaction product (expt 6) contains, in addition to **4** and **5**, significant amounts of 1,2-dimethyl-3,4-dihydronaphthalene (**6**), 2-methylnaphthalene (**7**), and 1,2-dimethylnaphthalene (**8**). The formation of dimethyl products may be attributed to the presence of very strong acidic sites,[5] which will foster dimethylation of 1-tetralone at C-2 and (along with available weak acidic sites) will effect subsequent reduction–rearrangement. The formation of methylnaphthalenes, on the other hand, may be attributed to the effects of elevated temperature *per se* in fostering catalyzed dehydroaromatization of intermediates (*vide infra*, reactions of 2,2-dimethyl-1-tetralone).

The reaction of **1** under the conditions of expt 1 or 5 could be conveniently employed for the practical syn-

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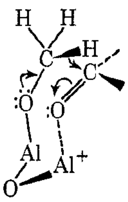
[11] For a stereochemical representation of such process in a similar case, see ref 5, Figure 2.

[12] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 23–26.

[13] A surface aluminum hydride is probably more nearly like an $(RO)_3AlH^-$ ion than an AlH_4^- ion. See H. C. Brown and H. R. Deck [*J. Amer. Chem. Soc.*, **87**, 5620 (1965)] for reduction of ketones by these species.

[14] Molecular hydrogen formed in the system (as, for example, *via* Scheme I) could remain available for reduction by dissociative chemisorption on the catalyst. *Cf.* H. Pines and J. Ravoire, *J. Phys. Chem.*, **65**, 1859 (1961); M. J. D. Low and E. S. Argano, *ibid.*, **70**, 3115 (1966).

[15] J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 456, 457; B. J. Yager and C. K. Hancock, *J. Org. Chem.*, **30**, 1174 (1965), and references cited therein. It might be noted that Scheme II depicts hydride transfer by means of a pseudocyclic eight-membered transition state involving two neighboring surface aluminum ions rather than by means of a six-membered cyclic transition state involving one coordinately bonded aluminum (as proposed for the Meerwein–Ponndorf–Verley reaction). While the latter type of transition state is not excluded for at least some surface sites, the stereochemistry of the alumina surface would seem to foster preferential formation of the former one, as indicated below. For a proposal on coordination of the aluminum atom in a "melt" of aluminum isopropoxide, see V. J. Shiner and D. Whittaker, *J. Amer. Chem. Soc.*, **91**, 394 (1969); I. J. Worrall, *J. Chem. Educ.*, **46**, 510 (1969).



[16] A. L. Wilds, *Org. Reactions*, **2**, 178 (1944). NOTE ADDED IN PROOF.—D. V. Ramana and C. N. Pillai [*Can. J. Chem.*, **47**, 3705 (1960)] have recently described such reductions by alcohols and alumina.

[17] 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 anion derived from 1-tetralone takes into account the expected decrease in the Coulomb integral which accompanies the increase in negative charge, but the S_r values calculated from this set do not include the effects of n electrons on the oxygen atom.

Table II

Alumina-Catalyzed Reactions of 2,2-Dimethyl-1-tetralone (**2**) with Methanol[a]

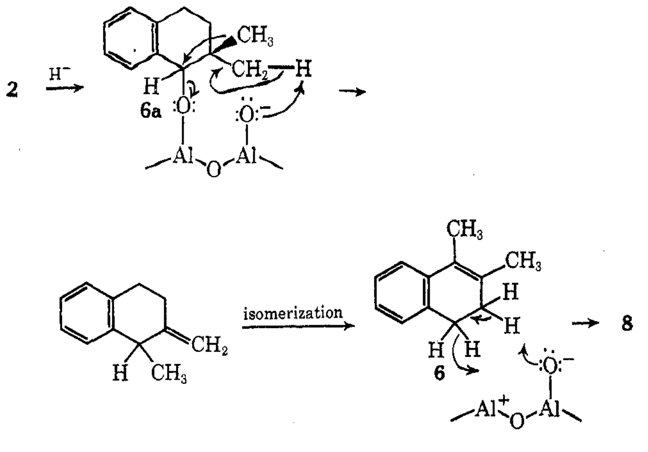
Expt no.	7	8	9	10	11
Catalyst	A	A	C	C	C
Reaction temp, °C	325	420	325	375	420
Conversion of **2**, mol %	87	100	68	89	100
Product component,[b] mol %					
2-Methyl-3,4-dihydronaphthalene (**5**)	1.6	0.3	43.7	15.2	12.5
1,2-Dimethyl-3,4-dihydronaphthalene (**6**)	50.7	7.8	8.3	9.0	9.1
2-Methylnaphthalene (**7**)	1.2	5.0	10.2	40.3	37.5
1,2-Dimethylnaphthalene (**8**)	30.5	80·1	3.4	19.5	37.7
Unidentified[c]	(1.2)	(4.5)	(1.0)	(1.6)	(2.1)

[a] Total quantities of 1.74 g (0.01 mol) of **2** and 17.5 g (0.55 mol) of methanol were used as starting materials in each experiment. [b] See footnote *b*, Table I, but for starting **2** (rather than for **1**). [c] Percentage by weight of total product.

thesis of 1,2-dihydronaphthalene or of 2-methyl-3,4-dihydronaphthalene, respectively. A decrease in the rate of addition of influent or an increase in the amount of catalyst (under conditions otherwise identical with those in expt 1) should improve the total conversion of **1**. It is presumed that these conditions would also be applicable to the syntheses of homologs of **4** and **5** with substituents in the aromatic ring.

Reactions of 2,2-Dimethyl-1-tetralone (2).—As seen from Table II, 1,2-dimethyl-3,4-dihydronaphthalene (**6**) and 1,2-dimethylnaphthalene (**8**) are the main products formed by reaction of **2** in the presence of methanol at 325° over catalyst A (expt 7). When the temperature is increased to 420° (expt 8) there is a sharp increase in the yield of **8** and a corresponding decrease in the yield of **6**. These results indicate that with A, **2** undergoes initial reduction–rearrangement to give **6**, which is subsequently dehydrogenated to 1,2-dimethylnaphthalene to an extent largely dependent on temperature. A similar dehydrogenation step probably serves to convert 2-methyl-3,4-dihydronaphthalene (**5**) into 2-methylnaphthalene (**7**). Transformation of **2** into **8** (*via* the alkoxide intermediate **6a** and the dihydronaphthalene **6**) is depicted in Scheme III.

Scheme III



Rearrangement of **6a** may involve γ-participation (as shown) in a manner similar to that proposed by Sanderson and Mosher[18] for base-catalyzed dehydration of neopentyl alcohol, with bromoform in aqueous potassium hydroxide, to give 2-methyl-1-butene as principal product. It has been noted that γ participation is unlikely to occur in acid-catalyzed reactions in solution but may occur readily in the dehydration of neopentyl alcohol with sodium-containing alumina or with alumina treated with piperidine.[19]

With catalyst C (expt 9–11) two temperature-dependent processes are apparent in the reaction of **2**. One is the aforementioned dehydroaromatization process, which becomes increasingly important as the temperature is raised (*cf.* total yield of **7** plus **8** with that of **5** plus **6** in each of the experiments). The other is loss of one of the geminal methyl groups, as indicated by the formation of **5** and **7**. In contrast to the dehydrogenation case, however, the relative extent of reduction–demethylation *vs.* reduction–rearrangement decreases with increase in temperature (*cf.* total yield of **5** plus **7** with that of **6** plus **8**). It is presumed that the latter temperature effect really operates through a change in the acidity of catalyst C (which increases with temperature in the range studied). Lending credence to this presumption is the fact that the strong acidic catalyst A fosters reduction–rearrangement (**2** → **6** and **8**), with very little attendant demethylation (*cf.* expt 7 and 9; 8 and 11). As noted before, it is believed that reduction–rearrangement occurs on (and presumably requires) a very strong acidic site (to which the substrate is bonded; *cf.* **6a**, Scheme III). In the absence of a large concentration of strong acidic sites, the alternative process of reduction–demethylation becomes important. Such reaction may involve initial demethylation of **2** to 2-methyl-1-tetralone, followed by reduction (as in Scheme II).

Reactions of 2,2,4,7-Tetramethyl-1-tetralone (3).—As seen from Table III, compound **3** undergoes aromatization at 420° over catalyst A (expt 14) to give 1,2,4,7-tetramethylnaphthalene (**10**) in nearly 90% yield. A small amount of the expected precursor, 1,2,4,7-tetramethyl-3,4-dihydronaphthalene (**9**), is also formed. As temperature is decreased the yield of **10** decreases whereas that of **9** increases. The ratio of **9** to **10**, however, is considerably lower than that of **6** to **8** under identical conditions (Table II, expt 7, 8). This would indicate that **9** undergoes dehydrogenation faster than **6**, probably as a result of the presence in **9** of a methyl substituent at C-4, which facilitates the loss of a hydride ion from this position (*cf.* conversion of **6** to **8** in Scheme III). It might be noted in this regard that methyl substituents enhance the rate of aromatization of hydroaromatic hydrocarbons with chromia–

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[18] W. A. Sanderson and H. S. Mosher, *J. Amer. Chem. Soc.*, **83**, 5033 (1961). For consideration of alternative mechanisms for the rearrangement process, see the preceding paper.[5]

[19] H. Pines and J. Manassen, *Advan. Catal.*, **16**, 49 (1966).

TABLE III
ALUMINA-CATALYZED REACTIONS OF 2,2,4,7-TETRAMETHYL-1-TETRALONE (**3**) WITH METHANOL[a]

Expt no.	12	13	14
Catalyst	A	A	A
Reaction temp, °C	325	375	420
Conversion of **3**, mol %	93	96	100
Product component,[b] mol %			
1,2,4,7-Tetramethyl-3,4-dihydronaphthalene (**9**)	26.5	10.4	4.9
1,2,4,7-Tetramethylnaphthalene (**10**)	58.0	76.2	89.3
1,3,6-Trimethylnaphthalene (**11**)[c]	6.2	5.9	4.0
Unidentified[d]	(1.1)	(1.5)	(1.3)

[a] The starting mixture used in each experiment consisted of 2 g (0.01 mol) of **3** and 20 g (0.63 mol) of methanol. [b] See footnote *b*, Table I, but for starting **3** (rather than for **1**). [c] Tentative structure, based on gas chromtographic behavior and mechanistic considerations only. [d] Percentage by weight of total product.

alumina catalysts.[20] Limited reduction–demethylation to a trimethylnaphthalene, probably **11**, is again found.

Experimental Section

Apparatus, Materials, and Procedure.—The apparatus and experimental procedure were essentially the same as previously used.[2-5] For each run 50 g of fresh alumina catalyst was employed in the form of a bed 25 cm long and situated in the isothermal section of the furnace. Catalysts A (from aluminum isopropoxide), C (Houdry hard alumina), and D (from sodium aluminate) were the same as used in previous studies.[2,5] The influent consisted of a solution of **1**, **2**, or **3** (0.02 mol) in methanol (1 mol) and was introduced into the reactor at a uniform rate (total addition time 1 hr 40 min) in a stream of nitrogen. Products were processed and analyzed as before.[3] Ultraviolet spectra were measured by means of a Cary Model 15 spectrophotometer. The nmr spectrum of **4** was measured with a Varian Associates HA-100 spectrometer.

Identification of Reaction Products.—2-Methylnaphthalene (**7**), 1,2-dimethylnaphthalene (**8**), and 1,2,4,7-tetramethylnaphthalene (**10**) were identified by comparison of infrared and nmr spectra, as well as vpc retention volumes, with those of authentic samples.[3] A minor product from **3** (Table III) was tentatively assigned the structure of 1,3,6-trimethylnaphthalene on the basis of gas chromatographic behavior on a Bentone-34 column.[21]

1,2-Dihydronaphthalene (**4**) was isolated in >99% purity by repeated vpc of products from expt 1, 2, and 6: bp 215–216° (760 mm) by micromethod;[22] n^{25}_{D} 1.5716 (lit.[23] bp 84–85° (12 mm); $n^{18.2}_{\mathrm{D}}$ 1.5832); uv max (95% EtOH) 258 mμ (ϵ 9590) and 264 (shoulder, 8960); ir (CS_2) 694 (*cis* CH=CH), 749, 785, 2840, 2895, 2950, and 3050 cm^{-1}; ir ($CHCl_3$) 1439, 1451, 1483, and 1640 cm^{-1} (C=C stretching); nmr (CCl_4) δ 6.7–7.3 (m, 4, aromatic protons at C-5 to C-8), ABC_2D_2 system (listed in order of decreasing δ values, where A = H-1, B = H-2, C = H-4, and D = H-3) 6.42 and 6.32 (d of t, 1, J_{AB} = 9.3 Hz, J_{AD} = 1.8 Hz, CH=CHCH$_2$), 5.90 (overlapping d of t, 1, J_{BD} = 4.3 Hz, CH=CHCH$_2$), 2.73 (unsymmetrical, partially split t, 2, J_{CD} = 8.3 Hz, protons at C-4), and 2.24 (m, 2, protons at C-3).

The absorption which is due to the C–H out-of-plane bending of the four vicinal aromatic hydrogens in **4** shows a characteristic splitting (bands at 749 and 785 cm^{-1}). A similar splitting is observed in the spectrum of 1,1,3-trimethyl-1,2-dihydronaphthalene[2] and in the spectra of 1,2,3,4-tetrahydronaphthalenes, which possess an unsubstituted aromatic ring.[24] The two sharp bands observed at 1451 and 1483 cm^{-1} could be tentatively assigned to the scissoring deformations of the two methylene groups in the hydroaromatic ring of **4**.[25]

2-Methyl-3,4-dihydronaphthalene (**5**) was isolated in >99% purity from the products of expt 6 and 7: bp 227–228° (760 mm) by micromethod; n^{25}_{D} 1.5721 (lit.[23] bp 63–65° (0.6 mm); n^{20}_{D} 1.5751); uv max (95% EtOH) 262 mμ (ϵ 12,000) and 268 (11,700); ir (CS_2) 726, 753, 842, 1653 (C=C stretching), 2830, 2880, 2930, and 3030 cm^{-1}; ir ($CHCl_3$) 1438 and 1485 cm^{-1}; nmr (CCl_4) δ 6.7–7.4 (m, 4, aromatic protons at C-5 to C-8), 6.14 (broad s, 1, CH=), A_2B_2 system 2.74 and 2.14 (two t, 2 each, J_{AB} = 8.0 Hz, CH$_2$ at C-4 and C-3, respectively), and 1.85 (s, 3, CH$_3$ at C-2).

Anal.[26] Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.92; H, 8.54.

Compared with the uv absorption of **4**, the maxima shown by **5** at 262 and 268 mμ are better resolved and shifted bathochromically by *ca.* 4 mμ. This shift is consistent with the presence of the methyl group on the conjugated system. The splitting of the aromatic C–H out-of-plane bending signal is less symmetrical (strong band at 753 cm^{-1}, weak band at 726 cm^{-1}) compared with that of **4**. A sharp band at 842 cm^{-1} can be assigned to out-of-plane bending of the C–H at the trisubstituted double bond.[27a] The position of the C=C stretching band (1653 cm^{-1}) fits the anticipated one for a trisubstituted double bond (*ca.* 1670 cm^{-1}) with a shift to lower frequency of 17 cm^{-1} owing to conjugation with the benzenoid ring.[27b]

1,2-Dimethyl-3,4-dihydronaphthalene (**6**) was isolated in >99% purity from the products of expt 6 and 7: bp 245–246° (760 mm) by micromethod; n^{25}_{D} 1.5750; uv max (95% EtOH) 263 mμ (ϵ 11,400) and 268 (11,300); ir (CS_2) 733, 760, 2835, 2885, and 2940 cm^{-1}; ir ($CHCl_3$) 1041, 1386, 1430, 1441, 1453, 1490, 1602, and 1645 cm^{-1} (C=C stretching); nmr (CCl_4) δ 6.8–7.3 (m, 4, aromatic protons at C-5 to C-8), A_2B_2 system 2.65 (t, 2, J_{AB} = 8.0 Hz, CH$_2$ at C-4), 2.13 (t partially overlapped by methyl signal, 2, CH$_2$ at C-3), 1.97 (s, 3, CH$_3$ at C-1), and 1.86 (s, 3, CH$_3$ at C-2).

Anal.[26] Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.90; H, 8.64.

As in the parent compound **4**, the aromatic C–H out-of-plane bending signal for **6** appears as a well-resolved doublet (strong bands at 733 and 760 cm^{-1}). The position of the C=C stretching band (1645 cm^{-1}) is normal for a conjugated, tetrasubstituted double bond.[27b]

An enriched (95% pure) sample of 1,2,4,7-tetramethyl-3,4-dihydronaphthalene (**9**) was obtained by vpc of the product from expt 12: uv max (95% EtOH) 263 mμ (ϵ 11,400) and 269 (11,300); ir ($CHCl_3$) 1648 cm^{-1} (C=C stretching, conjugated, tetrasubstituted double bond).[27b] The relative positions of the methyl substituents in **9** were confirmed by aromatization to 1,2,4,7-tetramethylnaphthalene (*vide infra*).

Aromatization of 4, 5, 6, and 9.—According to a standard procedure,[28] a solution of **4**, **5**, **6**, or **9** (1 mmol) and 0.5 g (2.2 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone in 50 ml of dry benzene was refluxed for 5 hr. The reaction mixture was diluted with petroleum ether (bp 30–60°), filtered, and chromatographed on Woelm neutral alumina with petroleum ether–benzene (1:1 by volume). The product was recovered by evaporation of the solvent. Compounds **4**, **5**, **6**, and **9** gave naphthalene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, and 1,2,4,7-tetramethylnaphthalene, respectively, in 90–94% yields. The products were shown to be isomerically pure by vpc and infrared analysis.

Registry No.—**1**, 529-34-0; **2**, 2977-45-9; **3**, 23230-33-3; **4**, 447-53-0; **5**, 2717-44-4; **6**, 5195-39-1; methanol, 67-56-1.

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