Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. II. Reactions of 1-Oxo-2,2-dimethyl-1,2-dihydronaphthalene, 1-Oxo-4,4-dimethyl-1,4-dihydronaphthalene, and 1-Methoxynaphthalene with Methanol[1a]

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The alumina-catalyzed reactions of 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene (IX), 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene (X), and 1-methoxynaphthalene (III) were studied at 320–420° in the presence of excess methanol. At 350° IX undergoes smooth reduction-rearrangement to form 1,2-dimethylnaphthalene in 84–98% yield (based on IX converted) in a reaction which has a low requirement for catalyst acidity. The reactions of X are distinctly dependent on catalyst acidity; 1,2,3,4-tetramethylnaphthalene and 1,2,3,4,6-pentamethylnaphthalene are main products (78–85 mol %) in the presence of strongly acidic alumina, whereas 1,1,3-trimethyl-1,2-dihydronaphthalene is formed as main product (>70% yield based on X converted) over weakly acidic catalysts. At 280–350° III yields oxygen-containing compounds (1-naphthol, methylated 1-naphthols, IX, and X) and methylnaphthalenes of the same array as obtained from 1-naphthol (I). Over weakly acidic catalysts at 280–350° the conversion of III is considerably lower than that of I, but this difference decreases with increasing catalyst acidity. At 420° over strongly acidic alumina the product distributions from III and I are nearly identical. Mechanistic aspects of the reactions are discussed.

In the preceding paper[2] it was shown that 1-naphthol (I) reacts with methanol at 350–550° in the presence of alumina catalysts to form relatively simple mixtures of methylnaphthalenes. At 275–300°, on the other hand, the reaction product contains 35–60% of oxygen-containing compounds, which include 2-methyl- and 4-methyl-1-naphthols, 2,4-dimethyl-1-naphthol, 1-methoxynaphthalene (III), 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene (IX), and 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene (X).[3] The present study is concerned with alumina-catalyzed reactions of methanol with compounds III, IX, and X in an effort to clarify the roles of the latter as possible intermediates in the ring-methylation process and to develop methods of preparation for selected polymethylnaphthalenes. Catalysts employed in the study were A (pure alumina, obtained by hydrolysis of aluminum isopropoxide),[2] C (Houdry hard alumina),[2] and D (alumina derived from potassium aluminate).[4] The apparatus and procedure were similar to those employed previously.[2] Reactions were carried out in a nitrogen atmosphere at temperatures of 280–420°. A fresh portion of alumina catalyst was used for each experiment. The molar ratio of methanol to III, IX, or X was 52:1 in all runs. Individual compounds were isolated from the products by preparative gas chromatography and identified by a combination of infrared and pmr spectral methods as well as, in most cases, by conversion into derivatives or by comparison with reference samples synthesized by independent means. Quantitative analysis of reaction products was carried out by means of gas chromatography.

Reactions of 1-Oxo-2,2-dimethyl-1,2-dihydronaphthalene (IX).—As seen from Table I, essentially only one product, 1,2-dimethylnaphthalene (XIV), is obtained from reaction of IX at 350° over the weakly acidic[4] catalysts D and C (expt 1 and 2). At this temperature a higher over-all conversion of IX is obtained with the strongly acidic[4] catalyst A (expt 3), but the product contains, in addition to XIV, small amounts of 2-methylnaphthalene (XIII), 1,2,3-trimethylnaphthalene (XVI), and 1,2,4-trimethylnaphthalene (XVII). XIV remains the predominant product at 420° with either catalyst C or A (expt 4 and 5), but the yield of trimethylnaphthalenes is somewhat increased.

The formation of 1,2-dimethylnaphthalene from IX involves the processes of oxygen elimination and skeletal rearrangement. Conceivably either process might occur first, or the two could occur simultaneously. A particularly attractive mechanism is presented in Scheme I where ketone IX is depicted as undergoing initial reduction (by hydrogen transfer from a reducing agent such as methanol or formaldehyde)[2] to carbinol XXXII, which subsequently undergoes dehydration with attendant neopentyl-type rearrangement of a methyl group from C-2 to C-1. In Scheme I the dehydration–rearrangement is represented as a concerted process with aspects of γ participation[5] and of anchimeric assistance by the migrating methyl group. The formation of a carbonium ion intermediate, in a stepwise process wherein both the hydroxide ion and (subsequently) the proton are lost from C-1, is also possible (*cf.* studies on dehydration of neopentyl alcohol over alumina).[5] Although XXXII could not be detected in the reaction products, it was found that this carbinol (synthesized separately in 97% yield by borohydride reduction of IX) does, indeed, undergo facile, quantitative conversion into XIV under the conditions of expt 2. Allylic rearrangement of XIVa to XIV should occur readily by proton transfer on the catalyst surface.

Alternatively, rearrangement might precede reduction, as shown in Scheme II. The mechanism is analogous to that proposed by Marvell and Magoon[6] for the dienone–phenol rearrangement of IX in sulfuric

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

[3] For simplicity, compounds and catalysts are designated by the same Roman numerals and capital letters, respectively, as used in part I.[2]

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

[5] H. Pines and J. Manassen, *Advan. Catal.*, **16**, 80 (1966); C. N. Pillai and H. Pines, *J. Amer. Chem. Soc.*, **83**, 3274 (1961).

[6] E. N. Marvell and E. Magoon, *ibid.*, **76**, 5118 (1954).

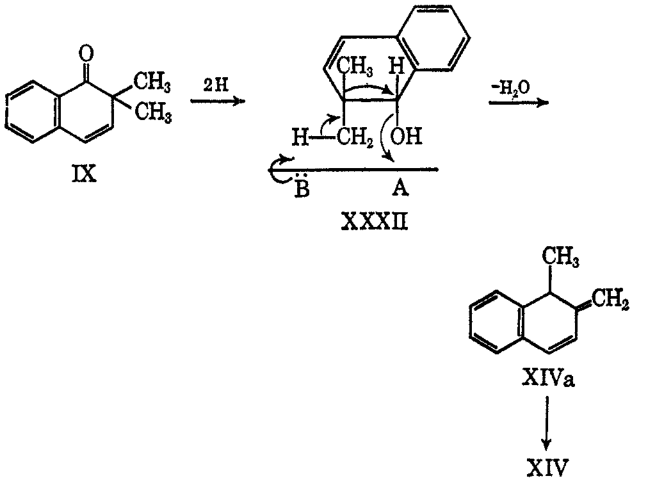
TABLE I

ALUMINA-CATALYZED REACTIONS OF 1-OXO-2,2-DIMETHYL-1,2-DIHYDRONAPHTHALENE (IX) IN THE PRESENCE OF METHANOL[a]

Expt no.	1	2	3	4	5
Catalyst	D	C	A	C	A
Reaction temp, °C	350	350	350	420	420
Conversion of IX, mol %	75	84	100	100	100
Product component,[b] mol %					
2-Methyl-N (XIII)	<0.1	0.1	4.6	4.5	4.0
1,2-Dimethyl-N (XIV)	74.5	83.5	84.0	74.0	76.0
1,2,3-Trimethyl-N (XVI)	<0.1	0.2	6.0	4.9	10.2
1,2,4-Trimethyl-N (XVII)	...	<0.1	1.7	1.3	2.8
Unidentified[c]	...	...	(2.8)	(5.3)	(5.8)

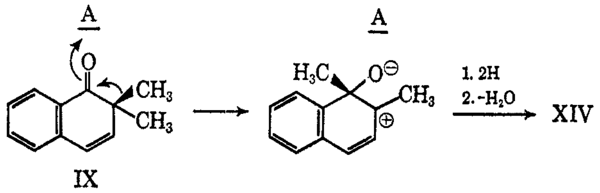
[a] Starting materials used in each experiment were 2 g (0.012 mol) of IX and 20 g (0.63 mol) of methanol. [b] Calculated on the basis of 100 mol of starting IX (including unreacted material). Differences between conversion and total product figures represent losses due to carbonaceous deposits on the catalyst. N = naphthalene. [c] Percentage by weight of total product. Includes unidentified chromatographic peaks and nondistillable residues.

SCHEME I



A = acidic site; B̈ = basic site (on the alumina surface)

SCHEME II

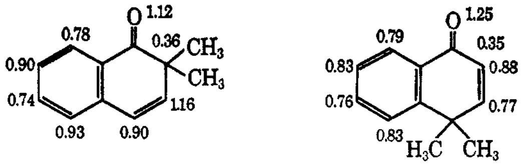


acid–acetic anhydride,[7] except that A is considered to be an acidic site on the alumina surface instead of a proton in solution. Also, the heterogeneous process leads to hydrocarbon XIV, while the homogeneous process gives, instead, 3,4-dimethyl-1-acetoxynaphthalene by reintroduction (from the solvent) of an oxygen function at a position *para* to the original OH.

1,2,3-Trimethylnaphthalene might result from initial direct electrophilic attack of a methyl group at C-3 of IX (see calculated superdelocalizability values in Scheme III[8]) followed by reduction–rearrangement of the hypothetical intermediate 1-oxo-2,2,3-trimethyl-1,2-dihydronaphthalene in the same manner as shown in Scheme I or Scheme II, or from initial rearrangement of IX to 2,3-dimethyl-1-naphthol (or its anion), methylation at C-2, and finally reduction–rearrangement as before. Several mechanistic pathways, each of low probability, could account for the small yields of 2-methylnaphthalene and of 1,2,4-trimethylnaphthalene.

SCHEME III

SUPERDELOCALIZABILITIES FOR ELECTROPHILIC ATTACK IN IX AND X(S_r, IN UNITS OF β_0^{-1})[a]



[a] See ref 8.

Reactions of 1-Oxo-4,4-dimethyl-1,4-dihydronaphthalene (X).—As seen from Table II the main products formed by the reaction of compound X with methanol over catalyst A (expt 6–9) are 1,2,3,4-tetramethylnaphthalene (XIX) and 1,2,3,4,6-pentamethylnaphthalene (XXII). These components are free from isomers. At 320° XIX is the major product, but its relative yield decreases whereas that of XXII increases with increasing reaction temperature, up to 375°. At 420° a significant amount of 1,2,3,4,6,7-hexamethylnaphthalene (XXIII) and small amounts of hepta- and octamethylnaphthalenes (Table II, footnote *d*) are also formed. At 375° (expt 8) the reaction can be conveniently employed as a method for the preparation of XXII, since the latter is easily freed (by distillation) from the small amounts of lower methylnaphthalenes present.

At 320° with the weakly acidic catalysts C and D the reaction is strikingly different from that found with catalyst A. 1,1,3-Trimethyl-1,2-dihydronaphthalene (XXXIII) is the main product obtained, whereas XIX and XXII are formed in only low yields with catalyst C (expt 10) or in trace amounts with catalyst D (expt 11). At 420°, on the other hand, XXXIII is produced in low yields while XIX is the main component and smaller amounts of XXII (expt 12 and 13) are also formed. This gross change in product composition may be ascribed to marked increase in the acidities of catalysts C and D with increase of temperature.[2]

A plausible mechanistic pathway for conversion of X into XIX and XXII is presented in Scheme IV. First it is assumed that X is transformed to a common intermediate VIIc (or VIIb) by a mechanism analogous to that proposed by Arnold, *et al.*,[9] for the dienone–phenol rearrangement of X in sulfuric acid–acetic anhydride solution to give 3,4-dimethyl-1-acetoxynaphthalene. In the present case, however, A, an acidic site on the catalyst surface, assumes the role of a proton (*vide supra*) and the oxygen function is not acetylated. Indeed, in expt 10, conducted at 320° with the weakly acidic catalyst C (Table II, footnote *e*), a small amount of naphthol VIIb was isolated. In the presence of a more acidic catalyst, however, desorption of VIIb or its anion VIIc may not occur to any appreciable extent (*cf.* the strong adsorption of 1-naphthol on alumina).[2] Instead, this adsorbed substrate should be readily susceptible to further methylation at the 2 and 7 positions[2] to give higher homologs of IX. Such

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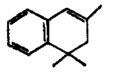
[7] E. N. Marvell and A. O. Geiszler, *J. Amer. Chem. Soc.*, **74**, 1259 (1952).

[8] For method of calculation, see ref 2. The parameters used for IX and X were $h_O = 1.0$, $k_{C-O} = 1.0$; *cf* A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p 123.

[9] R. T. Arnold, J. S. Buckley, and J. Richter, *J. Amer. Chem. Soc.*, **69**, 2322 (1947).

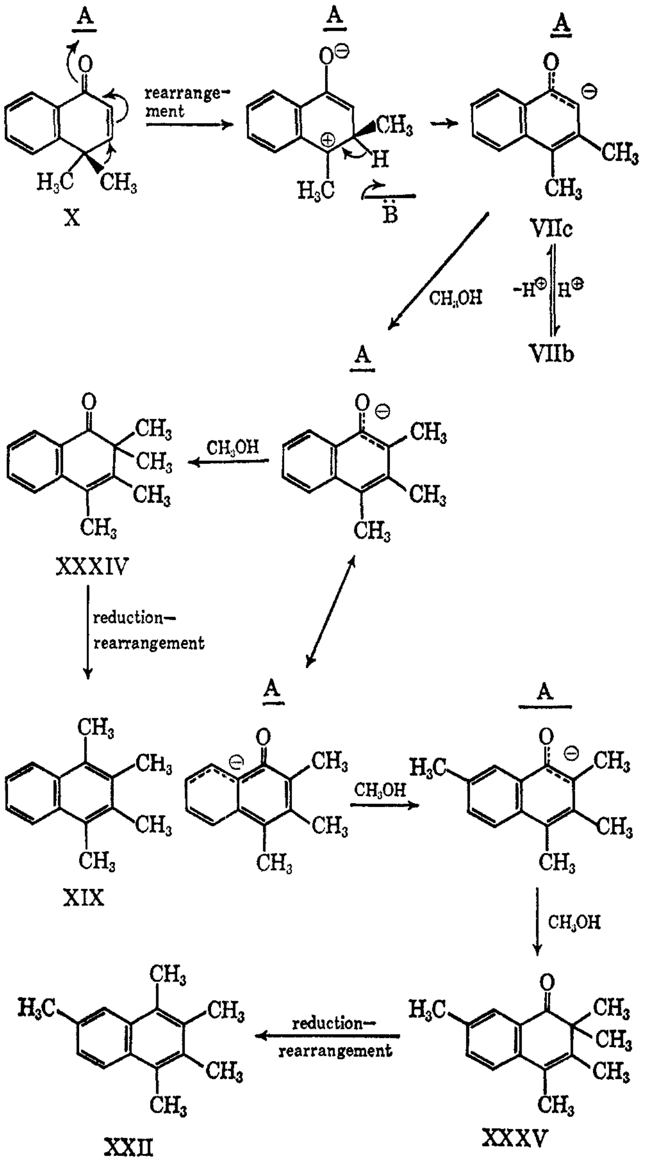
TABLE II

ALUMINA-CATALYZED REACTIONS OF 1-OXO-4,4-DIMETHYL-1,4-DIHYDRONAPHTHALENE (X) WITH METHANOL[a]

Expt. no.	6	7	8	9	10	11	12	13
Catalyst	A	A	A	A	C	D	C	D
Reaction temp, °C	320	350	375	420	320	320	420	420
Conversion of X, mol %	98	100	100	100	76	41	92	73
Product component,[b] mol %								
 (XXXIII)	3.7	2.0	1.3	Trace	54.5	37.2	4.5	5.2
1,2-Dimethyl-N (XIV)	...	1.0	2.9	0.5	...	...	...	...
1,2,3-Trimethyl-N (XVI)	2.4	2.8	3.4	0.8	Trace	...	3.5	3.4
1,2,4-Trimethyl-N (XVII)	0.7	0.9	0.6	0.8	...	...	...	...
1,2,3,4-Tetramethyl-N (XIX)	49.2	35.8	11.5	13.2	9.0	Trace	50.4	40.3
1,2,3,4,6-Pentamethyl-N (XXII)	34.5	45.2	71.6	64.4	4.6	...	26.1	18.9
1,2,3,4,6,7-Hexamethyl-N (XXIII)	...	...	Trace	13.0	...	...	...	...
Others[c]	(5.4)	(3.7)	(2.0)	(5.2)[d]	(9.7)[e]	(8.6)	(6.6)	(6.0)

[a] Total quantities of 2 g (0.012 mol) of X and 20 g (0.63 mol) of methanol were used as starting materials in each experiment. [b] See footnote *b*, Table I, but for starting X (rather than for IX). [c] Percentage by weight of total product. It includes unidentified chromatographic peaks and nondistillable residues. [d] Product contains 2.7 mol % of heptamethylnaphthalene and 1 mol % of octamethylnaphthalene, as based on gas chromatographic data only. [e] Of this total 23% is 3,4-dimethyl-1-naphthol (VIIb).

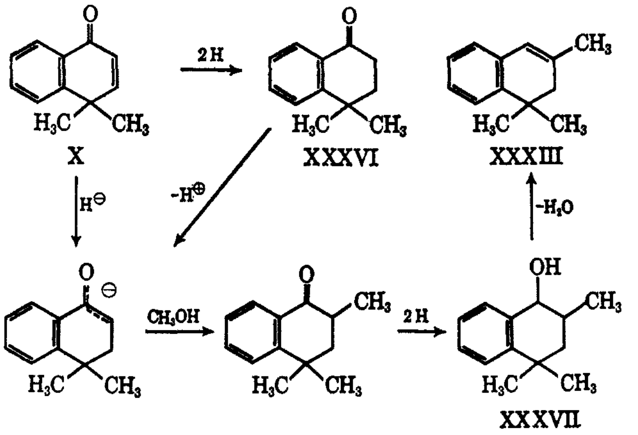
SCHEME IV



intermediate ketones (XXXIV and XXXV) were not isolated. However, they would be expected to undergo rapid reduction–rearrangement under the experimental conditions in analogy with IX (*vide supra*). The small amount of XVI may arise by methylation at C-2 followed by reduction–rearrangement (Scheme III).

In Scheme IV (and again in Scheme V) implications on the uncertain nature of the active methylating species have been avoided. The symbol CH_3OH is used merely to denote that methanol is the ultimate source of this electrophilic species.

SCHEME V



The operation of Scheme IV requires the presence of a catalyst of sufficiently high acidity in order to initiate the over-all process. At 320°, the very weakly acidic catalyst D would appear to be unable to effect molecular rearrangement of X, while the somewhat more acidic catalyst C can do so to a limited extent. Under the former conditions almost all of the X which reacts is converted into XXXIII, possibly *via* Scheme V. In analogy with the action of aluminohydrides in solution,[10] it is assumed that an alumina catalyst with sufficiently strong basic sites can initially furnish a hydride ion to the α,β-unsaturated ketone X (or, alternatively, abstraction of a proton may follow reduction of the C═C bond). Further methylation and reduction should give the intermediate carbinol XXXVII which could be dehydrated without skeletal rearrangement to XXXIII.[5] As a partial test of this mechanism the reaction of the saturated ketone

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[10] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 2.

TABLE III

ALUMINA-CATALYZED REACTIONS OF 1-METHOXYNAPHTHALENE (III) AND 1-NAPHTHOL (I) WITH METHANOL[a]

Expt no.	14	15	16	17	18	19
Substrate	III	I	III	I	III	I
Catalyst	C	C	C	C	A	A
Reaction temp, °C	280	280	350	350	420	420
Conversion of III or I, mol %	32	55	56	78	98	100
Product component,[b] mol %						
1-Methoxy-N (III)	(68.0)[c]	4.8	(44.0)[c]	1.0	(1.6)[c]	...
1-Methoxy-2-methyl-N (IV)	0.1	0.3	...	Trace	...	...
1-Naphthol (I)	2.4	(45.0)[c]	1.3	(22.0)[c]	...	...
2-Methyl-1-naphthol (V)[d]	5.5	14.5	7.2	10.3	...	...
1-Oxo-2,2-dimethyl-1,2-dihydro-N (IX)	3.6	4.4	2.2	1.6	...	...
1- and 2-methyl-N (XII, XIII)	1.5	0.6	1.9	3.4	2.8	3.1
1,2-Dimethyl-N (XIV)	12.1	17.0	21.0	23.6	15.7	15.5
1,2,3-Trimethyl-N (XVI)	0.5	0.9	0.7	1.7	4.1	4.0
1,2,4-Trimethyl-N (XVII)	1.8	3.5	5.7	8.0	5.8	5.7
1,2,7-Trimethyl-N (XVIII)	1.2	2.0	4.3	6.4	21.5	18.0
1,2,4,7-Tetramethyl-N (XXI)	0.3	1.8	4.7	7.8	16.9	15.6
1,2,3,4,6-Pentamethyl-N (XXII)	...	0.7	1.8	4.5	15.6	18.7
Others[e]	1.0	2.5	4.1	6.0	11.4[f]	15.1[g]
Unidentified[h]	(1.5)	(1.7)	(1.0)	(3.5)	(3.0)	(3.5)

[a] Total quantities of 0.012 mol of III (or I) and 20 g (0.63 mol) of methanol were used as starting materials in each experiment. [b] See footnote *b*, Table I, but for starting III or I (rather than for IX). [c] Unreacted starting material. [d] Includes small amounts of 4-methyl-1-naphthol. [e] Includes 2,4-dimethyl-1-naphthol, 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene, and other methylnaphthalenes. [f] Includes 3.3 mol % of 1,2,3,4,6,7-hexamethylnaphthalene (XXIII). [g] Includes 5.6 mol % of XXIII. [h] See footnote *c*, Table I.

XXXVI in the presence of methanol was studied under the conditions of expt 10. XXXVI gave a product which contained XXXIII as the main component (78% yield, based on XXXVI converted). The structure of XXXIII was established by spectral methods and by aromatization to 1,2,3-trimethylnaphthalene (93% yield) upon refluxing with a benzene solution of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). If the lone methyl group had been located at C-1 rather than at C-2 (in XXXVII) the aromatized product should have been 1,2,4-trimethylnaphthalene, instead.

It is apparent that X could serve as a convenient precursor for the synthesis of XXXIII on a preparative scale. Moreover, X should be useful as a substrate for evaluation of the relative acidities of alumina catalysts,[4] as adjudged by product compositions under the conditions of the experiments in Table II.

Reactions of 1-Methoxynaphthalene (III).—Table III summarizes the results of a comparative study of the reactions of methanol with III and with 1-naphthol (I). The higher conversion of I and some differences in the composition of products in expt 15, 17, and 19, as compared with previous results,[2] are due to the use of higher ratios of catalyst–naphthol and of methanol–naphthol in the present study. Under conditions of low acidity (catalyst C, 280–350°) III yields an array of oxygen-containing compounds, *e.g.*, I, V, and IX, and methylnaphthalenes closely similar to that obtained from I. However, the yields of individual components and the depth of methylation in the reactions with III are markedly lower than those with I (*cf.* expt 14–17). The formation of 1-naphthol in expt 14 and 16 shows that III undergoes demethylation at reaction conditions. Further, the formation of only trace amounts of 1-methoxy-2-methylnaphthalene (IV) and the absence of other products containing a methoxy group indicates that III is not methylated *per se*. More likely, III is first cleaved on the alumina surface (with or without the intervention of another chemical entity) to give I or its anion, which then reacts in the usual manner. The significantly lower conversion of III at 280–350° implies that the cleavage reaction of III is slow compared to methylation of I. Alternatively, but less likely, III may first rearrange to 2-methyl-1-naphthol in a step which proceeds at a slower rate than subsequent methylation.

Over catalyst A at 420°, the product compositions from III and I are nearly identical (*cf.* expt 18 and 19). This is consistent with the expected increase in the rate of cleavage or of rearrangement of III with increased catalyst acidity and higher temperature. It is apparent that at such conditions the preparation of methylnaphthalenes by the alumina-catalyzed methylation process can proceed with equal facility from either I or III as a substrate.

Experimental Section[11]

Apparatus, Catalysts, and Procedure.—The apparatus and experimental procedure were essentially the same as previously employed,[2] except that experiments were carried out on a smaller scale and the catalyst–substrate and methanol–substrate ratios were higher than those used in the study of 1-naphthol.[2] For each run 35 g of fresh alumina catalyst was used in the form of a bed 18 cm long and supported in the isothermal section of the reactor. In addition to the previously described catalysts A (from aluminum isopropoxide) and C (Houdry hard alumina)[2] a third alumina catalyst (D) was also used. D was prepared by solution of aluminum (99.9% pure) in aqueous potassium hydroxide, neutralization of excess alkali with nitric acid, and, finally, precipitation of aluminum hydroxide with carbon dioxide.[4] All catalysts were activated *in situ* as previously.[2] The influent consisted of a solution of III, IX, or X (0.012 mol) in methanol (20 g, 0.63 mol) and was introduced into the reactor at a uniform rate over a period of 2 hr. Products were processed and analyzed as before.[2]

Isolation and Identification of Reaction Products.—1-Naphthol, methylated 1-naphthols (V–VIIa), 1-methoxynaphthalene, and methylnaphthalenes (XII–XIV, XVI–XIX, XXI–XXIII) were identified by comparison of pmr and infrared spectra, as well as vpc retention volumes, with those of authentic samples.[2]

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(11) Unless otherwise noted, analytical methods for vpc and for infrared and pmr spectra were the same as in ref 2. Ultraviolet spectra were measured by means of a Cary Model 11 spectrophotometer.

3,4-Dimethyl-1-naphthol (VIIb) was isolated by gas chromatography of the combined acidic fractions of several runs made under the conditions of expt 10. It was recrystallized from 80% ethanol: mp 121–122.5° (lit.[7] mp 120–122°); pmr spectrum (in $CDCl_3$), two singlets, 3 H each (δ 2.32, 2.45) methyl groups; broad singlet, 1 H (5.1) OH; singlet, 1 H (6.52) proton at C-2; multiplet, 4 H (7.1–8.3), aromatic protons at C-5 to C-8; $\nu_{\max}^{CS_2}$ [intensities: (s) strong, (m) medium] 758 s, cm^{-1}, 838 m, 1081 m, 1087 m, 1151 m, 1226 s; $\nu_{\max}^{CHCl_3}$ 1357 m cm^{-1}, 1366 m, 1390 s, 1464 m, 1521 m, 1600 s, 1630 m, 2945 m, 3030 m, 3610 s; identical in the spectral patterns with an authentic synthetic sample;[9] converted into 2-bromo-3,4-dimethyl-1-naphthol, mp 101–102° (lit.[9] mp 101.5–102.5°). The infrared absorption bands of VIIb at 758 and 838 cm^{-1} are assigned to CH out-of-plane deformation of the vicinal hydrogens in the unsubstituted ring and of the lone hydrogen at C-2, respectively.

1,1,3-Trimethyl-1,2-dihydronaphthalene (XXXIII) was isolated as a colorless liquid by preparative vpc from the products of expt 10 and 11: bp 249° (751 mm) by micromethod;[12] n^{20}_{D} 1.5536; pmr spectrum, singlet, 6 H (δ 1.22) geminal dimethyl group; broadened singlet, 3 H (1.86) vinylic methyl group; broadened singlet, 2 H (2.08) methylene group; broadened singlet, 1 H (6.13) vinylic proton; and multiplet, 4 H (6.7–7.3) aromatic protons; $\nu_{\max}^{CS_2}$ 752 s cm^{-1}, 760 m, 843 m, 887 m, 1047 m, 1142 m; $\nu_{\max}^{CCl_4}$ 1365 m cm^{-1}, 1447 s, 1489 s, 1662 m, 2920 m, 2980 s; $\lambda_{\max}^{EtOH}$ 263 mμ (log ϵ 4.10), 269 (4.11).

Anal.[13] Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.31; H, 9.27.

The CH out-of-plane deformation of the four vicinal aromatic hydrogens of XXXIII shows a characteristic splitting (bands at 752 and 760 cm^{-1}). Similar doublets at *ca.* 735 and 753 cm^{-1} are observed in the spectra of 1,2,3,4-tetrahydronaphthalenes which possess an unsubstituted aromatic ring.[14] The similarity of the ultraviolet absorption spectrum of XXXIII to that of 1,2-dihydronaphthalene (partially resolved maxima at *ca.* 260 and 265 mμ, log ϵ *ca.* 4),[15] but shifted bathochromically by 3–4 mμ, is consistent with conjugation of the carbon–carbon double bond with the benzenoid ring and with the location of a methyl substituent on this double bond. The C=C stretching vibration at 1662 cm^{-1} corroborates these structural assignments since its position is normal for a conjugated, trisubstituted double bond (*i.e.*, ν somewhat less than 1670 cm^{-1}) and its intensity is enhanced compared to that of a nonconjugated double bond.[16]

Aromatization of XXXIII.—According to a general procedure,[17] a solution of 172 mg (1 mmol) of preceding XXXIII 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 vol) as eluent. Evaporation of the effluent left 162 mg (93%) of 1,2,3-trimethylnaphthalene, identified by direct comparison of its infrared spectrum and vpc retention volume with those of a reference sample.[2]

Reaction of 1-Oxo-4,4-dimethyl-1,2,3,4-tetrahydronaphthalene (XXXVI) with Methanol.—A solution of 0.8 g of 1-oxo-4,4-dimethyl-1,2,3,4-tetrahydronaphthalene[9] [pmr spectrum, singlet (δ 1.30) geminal methyl groups; symmetric A_2B_2 multiplet centered at δ 2.23 ($\Delta\delta_{AB} = 39$ cps, $J_{AB}/\Delta\delta_{AB} \simeq 0.2$)[18] dimethylene group; multiplet (6.9–7.6) aromatic protons probably at C-5 to C-7; multiplet (7.7–8.0) aromatic proton probably at C-8] in 8 g of methanol was passed over catalyst C at 320° under conditions identical with those in expt 10, Table II. Conversion of the ketone was 68%. The total reaction product (0.55 g, excluding starting materials) was found by vpc to contain 78% by weight of XXXIII, plus unidentified components.

1-Hydroxy-2,2-dimethyl-1,2-dihydronaphthalene (XXXII).—To a stirred solution of 0.85 g of 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene[2] in ethanol was added (over a period of 10 min) a suspension of 0.1 g (excess) of sodium borohydride in the same solvent. The mixture was stirred for 2.5 hr, and the solvent was evaporated *in vacuo*. The residue was treated with water, left overnight, and then extracted with ether. Evaporation of the dried ether extract gave 0.84 g (97%) of viscous, colorless liquid, 98% pure as determined by vpc with a stationary phase of 550-DC silicone oil (10% by wt) on Chromosorb W at 150° and high helium flow rate (>200 cc/min). Preparative vpc gave a chromatographically pure sample: n^{25}_{D} 1.5665; pmr spectrum, two singlets, 3 H each (δ 0.95, 1.00) geminal methyl groups; broadened doublet, 1 H (δ 2.84, $J = 6$ cps) proton at C-1; broadened doublet, 1 H (δ 4.28, $J = 6$ cps) OH proton; AB system, 2 H (δ_A 5.62, δ_B 6.22, $J_{AB} = 9.5$ cps) vinylic protons at C-3 and C-4; multiplet 4 H (6.7–7.5) aromatic protons; $\nu_{\max}^{CS_2}$ 697 m cm^{-1}, 751 m, 770 s, 779 s, 790 s, 836 m, 948 m, 999 s, 1027 m, 1048 s, 1360 m, 1376 s; $\nu_{\max}^{CHCl_3}$ 1468 s, and 1487 s cm^{-1}; $\nu_{\max}^{CS_2}$ 2878 m cm^{-1}, 2936 m, 2973 s, 3035 m, 3490 m, 3604 m.

Anal.[19] Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.91; H, 8.18.

Dehydration of XXXII on Alumina.—A solution of 0.6 g of XXXII in 6 g of methanol was passed (at constant rate over a period of 35 min) through a column containing 25 g of catalyst C at 350°. This was followed by 50 ml of benzene. The combined organic effluent was separated from water, dried, and evaporated to leave 0.5 g (93%) of 1,2-dimethylnaphthalene, free of isomers as based on vpc with a stationary phase of Bentone 34 (10% by wt) and 550-DC silicone oil (5%) on Chromosorb W; identical in infrared spectrum and vpc retention volume with a reference sample.

Registry No.—III, 2216-69-5; VIIb, 16020-34-1; IX, 16020-15-8; X, 16020-16-9; methanol, 67-56-1; XXXII, 16020-36-3; XXXIII, 16020-37-4; XXXVI, 2979-69-3.

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