at the reflux temperature for 15 hr, and the cooled solution was poured into water (500 ml). The resulting mixture was extracted with three 150-ml portions of ether. The combined ether extracts were dried ($MgSO_4$) and concentrated on a rotary evaporator to give 70.0 g of a clear liquid, $n^{25}D$ 1.4468. Distillation of the liquid gave 2H-cyclooctapyrazole (29.70 g, 64%) as a clear viscous oil [bp 128–129° (0.10 mm), $n^{25}D$ 1.5332]. The oil crystallized upon standing overnight to give a white solid, mp 45°.

Anal. Calcd for $C_9H_{14}N$: C, 71.95; H, 9.39; N, 18.65. Found: C, 71.67; H, 9.33; N, 18.51.

The infrared spectrum of the product follows: ν_{N-H} (3150 cm^{-1}), $\nu_{=CH}$ (3050 cm^{-1}), ν_{CH_2} (2900–2850 cm^{-1}), $\nu_{C=N}$ (1590 and 1575 cm^{-1}). The nmr spectrum of **22** follows: CH_2 (broad, τ 8.53, wt 12), CH_2—C=C (complex multiplet, τ 7.38, wt 4), =C(H)—N (singlet, τ 2.85, wt 1) and N-*H* (broad, τ 3.34, wt 1). The ultraviolet spectrum of **25** showed $\lambda_{max}^{95\% EtOH}$ 222 mμ (ε 13,950).

Crystalline 2H-cyclooctapyrazole picrate (mp 133.5–134.0°) was recovered in 77% yield after treatment of **22** with picric acid solution.

Anal. Calcd for $C_{15}H_{17}N_5O_7$: C, 47.49; H, 4.52; N, 18.46. Found: C, 47.32; H, 4.53; N, 18.19.

1-Acetoxy-7,7-dichlorobicyclo[4.1.0]heptane (19b). **A.**—1-Cyclohexenyl acetate (18.80 g, 0.135 mol) and phenyl(trichloromethyl)mercury (74.95 g, 0.188 mol) were stirred in benzene (200 ml) at the reflux temperature for 48 hr. The reaction mixture was cooled to room temperature and filtered to give phenylmercuric chloride (50.5 g, 86%). The filtrate was concentrated on a rotary evaporator and the residue was distilled to give **19b** [22.56 g, 75%, bp 128–131° (0.80 mm), $n^{25}D$ 1.4892].

Anal. Calcd for $C_9H_{12}Cl_2O_2$: C, 48.45; H, 5.42; Cl, 31.79. Found: C, 48.52; H, 5.43; Cl, 31.43.

The infrared spectrum of the product follows: ν_{CH_3} (2920 and 2850 cm^{-1}), $\nu_{C=O}$ (1755 cm^{-1}), and ν_{C-O-C} (1220 cm^{-1}). The nmr spectrum of **19b** follows: OCOCH_3 (singlet, τ 7.98) and CH_3 (broad, τ 7.50–8.83).

B.—A solution of 1-cyclohexenyl acetate (8.00 g, 0.057 mol) and sodium trichloroacetate (32.50 g, 0.114 mol) in 1,2-dimethoxyethane (125 ml) was heated at the reflux temperature for 5 hr. The solution was concentrated on a rotary evaporator. Distillation of the residue gave **19b** [2.24 g, 18%, bp 93–108° (1.4 mm), $n^{25}D$ 1.4918]. The infrared spectrum of the product was essentially identical with a sample of **19b** prepared as described above.

Reaction of 1-Acetoxy-7,7-dichlorobicyclo[4.1.0]heptane (19b) with Hydrazine.—Hydrazine (95%, 2.72 g, 0.081 mol) dissolved in ethanol (10 ml) was added dropwise with cooling to a solution of **19b** (4.00 g, 0.018 mol) in ethanol (20 ml). The mixture was heated at the reflux temperature for 1 hr, cooled to room temperature, and poured into water (50 ml). The solution was extracted with three 50-ml portions of ether. The dried ($MgSO_4$) ether extracts were concentrated to give 0.68 g of a red oil, $n^{24}D$ 1.5592. The nmr spectrum of the product follows: CH_2 (broad, τ 8.28), CH_2—C=C (complex τ 7.42), and =C—*H* (singlet, τ 2.84). This suggested that the product was impure 4,5,6,7-tetrahydroindazole.

The aqueous layer from the extraction was acidified with 6 *N* HCl solution, and extracted with three 50-ml portions of ether. The dried ($MgSO_4$) ether extracts were concentrated to give 30 mg of black tarry material which was ultimately discarded.

The aqueous layer was adjusted to pH 7 with dilute sodium hydroxide solution and extracted with three 50-ml portions of chloroform. The water layer was saturated with solid potassium carbonate and extracted with 50 ml of chloroform. The combined chloroform extracts were dried ($MgSO_4$) and concentrated to give slightly impure **26** (0.90 g, 41%, mp 65–70°; lit.[25] mp 79.0–79.5°). The nmr spectrum of the product follows: CH_2 and CH_2—C=C (broad, τ 7.4–9.0), =C—*H* (singlet, τ 2.70). The infrared spectrum of the product was essentially identical with that of an authentic sample[21] of **26**, and a mixture melting point of the product with authentic **26** was undepressed.

Registry No.—**12**, 15984-02-8; **13**, 15984-03-9; **15a**, 15984-04-0; **15b**, 15984-05-1; **19b**, 15984-06-2; **20**, 14605-45-9; **21**, 15984-08-4; HCl of **21**, 15984-09-5; **22**, 15984-10-8; HCl of **22**, 15984-11-9; picrate of **22**, 15984-12-0.

(25) C. Ainsworth, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 536.

Alumina-Catalyzed Reactions of Hydroxyarenes and Hydroaromatic Ketones. I. Reactions of 1-Naphthol with Methanol[1a]

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The alumina-catalyzed reactions of 1-naphthol (I) with excess methanol were studied as a function of temperature (275–550°) and catalyst acidity. Three types of reactions were observed: (a) ether formation, (b) ring methylation, and (c) self-condensation of I. Formation of 1-methoxynaphthalene (type a) is significant only at 275–300° over catalysts of low acidity. At 350–550° the predominant reaction (60–95%) is ring methylation with concurrent elimination of the arenolic group to give the following main products (maximal yields of 12–30 mol %): 1,2-dimethylnaphthalene, 1,2,4- and 1,2,7-trimethylnaphthalenes, 1,2,4,7-tetramethylnaphthalene, and 1,2,3,4,6-pentamethylnaphthalene. Smaller amounts of 2-methylnaphthalene, 1,2,3-trimethylnaphthalene, 1,2,3,4-tetramethylnaphthalene, and 1,2,3,4,6,7-hexamethylnaphthalene are also produced. Up to 420° the average depth of methylation was found to increase with increasing acidity of the alumina. Oxygen-containing compounds are formed in yields of 35–60% at 275–300°, but are not found above 420°. They include 2- and 4-methyl-1-naphthols, 2,4-dimethyl-1-naphthol, 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene, and 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene. The preferential methylation of I at C-2 and C-4 observed at 275–300° is in agreement with reactivity indices for the molecule, as calculated by the HMO method. At 470–550° I undergoes some self-condensation to give perylene. Spectral properties of isolated compounds are reported. An unambiguous synthesis of 1,2,4,7-tetramethylnaphthalene was developed.

The alumina-catalyzed reaction of phenol with methanol is employed as a convenient method for the preparation (in 67% yield) of hexamethylbenzene (II).[2] This reaction was first reported by Briner, Plüss, and Paillard,[3] who worked with a flow system mainly at 410–430° and used a large excess of methanol (relative to phenol) in the influent mixture. Compound II was similarly obtained[3] when phenol was replaced with *o*- or *p*-cresol, 3,5- or 4,5-dimethylphenol, or resorcinol. However, benzene did not react with methanol under

(1) (a) This investigation was supported by Research Grants No. CA-5969 from the National Cancer Institute and No. GM 12730 from the National Institute of General Medical Sciences, U. S. Public Health Service. (b) On leave from the Department of Chemistry, Weizmann Institute of Science, Rehovoth, Israel. (c) Research Assistant 1964–1967.

(2) N. M. Cullinane, S. J. Chard, and C. W. C. Dawkins, "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, pp 520, 521.

(3) E. Briner, W. Plüss, and H. Paillard, *Helv. Chim. Acta*, **7**, 1046 (1924).

the same conditions.[4] These results indicate that the phenolic group plays an essential role in the methylation reaction. Cullinane and Chard[5] studied the phenol–methanol reaction at milder temperatures and with nearly equimolar concentrations of the reactants. Low temperatures (200°) favored the formation of anisole, whereas the main products at 345° were *o*- and *p*-cresol, xylenols, and some polymethylphenols plus a small amount of II. It thus appears that the formation of II is a stepwise reaction involving oxygen-containing intermediates. More recently, Landis and Haag[6] reported that the product of the reaction at 400° contains in addition to II, about 9% of pentamethylbenzene. They also claimed that pentamethylbenzene is readily converted into II by reaction with methanol under the same conditions.[7] Briner, *et al.*,[3] and Plüss[8] found that 1- and 2-naphthols (but not naphthalene) react with excess methanol at 420–450° to produce a mixture of alkylnaphthalenes. With the exception of a single tetramethylnaphthalene, however, no individual compounds were isolated from these reactions.

This paper is concerned with a study of the alumina-catalyzed reaction of 1-naphthol (I) with methanol as functions of reaction temperature and catalyst acidity. Since recent studies by Pines, *et al.*,[9] Tung and McIninch,[10] and MacIver, *et al.*,[11] have shown that the direction and/or the rate of alumina-catalyzed reactions are dependent on catalyst acidity, three different types of alumina were used. Catalyst A (sodium-free) was obtained by hydrolysis of purified aluminum isopropoxide. It has been classified as strongly acidic since it shows high activity for the skeletal isomerization of cyclohexene[9] and for the cracking of cumene and 1-hexene above 400°.[10] Catalyst B (Harshaw alumina, containing *ca.* 0.4% sodium) has been classified as weakly acidic since it is effective for the isomerization of 3,3-dimethyl-1-butene to 2,3-dimethylbutenes but is ineffective for isomerizing the latter to 2-methylpentene, or of cyclohexene to methylcyclopentene.[9] Catalyst C (Houdry alumina, containing *ca.* 0.4% sodium) was classified as virtually nonacidic at temperatures below 350° where it showed little effectiveness for the isomerization of 3,3-dimethyl-1-butene.[9] In the present study, however, catalyst C exhibited considerable activity for methylation at 420–550°. Catalysts were preactivated by an identical procedure (see Experimental Section). The crystalline phases present in the three catalysts were reported[9] to be η, γ, and γ plus χ, respectively. Reactions were conducted in nitrogen atmosphere, in a flow system containing a fixed catalyst bed, at several temperatures in the range of 275–550° and with a molar ratio of methanol to 1-naphthol in the influent of 10:1 in most experiments. Products were isolated from the effluent mixtures by preparative gas chromatography and were identified by a combination of infrared and pmr spectral methods, as well as (in many cases) by direct comparison with authentic reference samples. Quantitative analyses of the reaction mixtures were conducted by means of gas chromatography. Data obtained are presented in Table I.

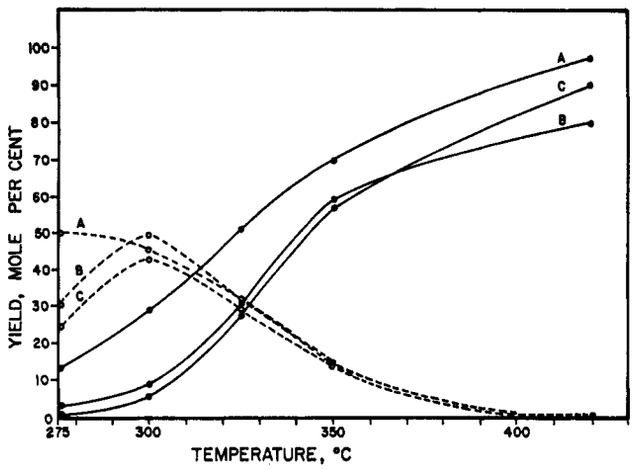


Figure 1.—Relative extents of formation of (a) methyl-substituted naphthols plus oxo compounds (broken curves) and (b) methyl-substituted naphthalenes (continuous curves) over catalysts A, B, and C, as functions of temperature. Data at 325° (not given in Table I) are also included.

Results

As seen from the table there are four types of products formed by the reaction of 1-naphthol with methanol in the range of temperatures studied: naphthyl ethers (III and IV), methylated naphthols (V–VII), methylated oxodihydronaphthalenes (VIII–X), and methylnaphthalenes (XII–XXV). Ether formation is observed in limited yields (up to 16 mol %) only at low temperatures (not >350°). The relative importance of this reaction decreases with increased acidity of the catalyst (*cf.* expt 1–3 and also 4–6, catalyst acidity A > B > C). However, the main reaction at 275–300° is ring methylation (largely, if not entirely, at the 2 and 4 positions) without loss of the oxygen atom from the molecule (see compounds V–X). Smaller amounts of certain methylated naphthalenes (particularly 1,2-dimethyl, 1,2,4-trimethyl, and 1,2,3-trimethyl, in order of decreasing yield) are also produced. As the reaction temperature is increased above 300° the yield of oxygen-containing products falls essentially to zero (attained at *ca.* 420°) whereas the yield of methylnaphthalenes increases rapidly to a maximum of *ca.* 75–95% at 420–470° (see Figure 1). This trend is observed over all of the catalysts, though the maximum yield of oxygen-containing compounds is attained at a lower temperature (possibly <275°) for catalyst A than for the less acidic catalysts B and C. It might be noted that in the low-temperature range (especially at 275–325°) the yield of methylnaphthalenes is also highest with catalyst A. The characteristics of the curves in Figure 1 imply that methyl-substituted naphthols and oxo compounds are probable intermediates in the formation of methylnaphthalenes.

As the reaction temperature is increased from 275 to 550° the composition of the methylnaphthalene product changes. In over-all result the average number of C-methyl groups per naphthalene or hydronaphthalene

(4) A check in our laboratory showed that toluene likewise does not react under similar conditions.

(5) N. M. Cullinane and S. J. Chard, *J. Chem. Soc.*, 821 (1945).

(6) P. S. Landis and W. O. Haag, *J. Org. Chem.*, **28**, 585 (1963).

(7) We have been unable to confirm this claim in our laboratory. Details will be reported in a later paper.

(8) W. Plüss, *Helv. Chem. Acta*, **8**, 507 (1925).

(9) H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, **82**, 2471, 2488 (1960); **83**, 2847 (1961); H. Pines and C. N. Pillai, *ibid.*, **82**, 2401 (1960); **83**, 3270, 3274 (1961); K. Watanabe, C. N. Pillai, and H. Pines, *ibid.*, **84**, 3934 (1962); H. Pines and J. Manassen, *Advan. Catal.*, **16**, 49 (1966).

(10) S. E. Tung and E. McIninch, *J. Catal.*, **3**, 229 (1964).

(11) D. S. MacIver, W. H. Wilmot, and J. M. Bridges, *ibid.*, **3**, 502 (1964).

TABLE I

COMPOSITION OF PRODUCTS OBTAINED FROM THE ALUMINA-CATALYZED REACTIONS OF 1-NAPHTHOL (I) WITH METHANOL[a]

Experiment no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Catalyst	C	B	A	C	B	A	C	B	A	C	B	A	A	C	B	A	C	B	A
Reaction temp, °C	275	275	275	300	300	300	350	350	350	420	420	420	420	470	470	470	550	550	550
Conversion of I, mol %[b]	37	42	67	66	69	79	75	76	87	~100	85	100	100	100	86	100	100	94	100
Product components,[b,c] mol %																			
1-Methoxy-N (III)	11.0	5.2	2.5	11.7	5.5	2.6	0.7	Trace	...	...	...	...	...	...	...	...	...	...	...
1-Methoxy-2-methyl-N(IV)	0.9	1.5	1.2	4.3	3.5	1.7	0.2	Trace	...	...	...	...	...	...	...	...	...	...	...
2-Methyl-1-naphthol (V)	21.5	27.2	33.2	33.2	37.0	26.5	8.9	10.2	9.6	...	0.7	...	...	...	...	...	...	...	...
4-Methyl-1-naphthol (VI)	0.4	1.3	4.0	2.0	3.8	4.5	1.3	2.1	3.0	...	0.2	...	...	...	...	...	...	...	...
Dimethylnaphthols (VII)[d]	0.1	0.5	1.4	2.3	5.4	0.8	1.0	1.2	0.5	...	0.1	...	...	...	...	...	...	...	...
1-Oxo-2-methyl-1,2-dihydro-N (VIII)[e]	0.2	0.2	0.8	0.3	0.2	1.1	0.6	0.1	0.5	Trace	...	...	...	...	...	...	...	...	...
1-Oxo-2,2-dimethyl-1,2-dihydro-N (IX)	1.9	2.1	7.3	4.9	2.4	8.7	1.5	0.4	0.4	Trace	0.2	0.1	0.1	...	...	...	...	...	...
1-Oxo-4,4-dimethyl-1,4-dihydro-N (X)	...	Trace	2.6	Trace	0.9	3.8	0.6	0.1	0.1	Trace	Trace	...	...	...	...	...	...	...	...
Naphthalene (XI)	...	...	...	...	...	0.1	1.5	0.9	1.5	2.8	1.7	1.3	0.8	3.4	1.8	0.4	1.3	2.6	2.7
1-Methyl-N (XII)	...	...	...	...	...	...	0.8	1.3	1.3	1.6	1.1	1.4	0.9	1.4	1.1	0.6	1.8	2.7	2.7
2-Methyl-N (XIII)	...	...	0.1	0.1	0.1	0.2	3.4	3.4	2.2	3.5	3.1	1.6	1.1	2.6	2.7	1.2	4.7	6.0	6.2
1,2-Dimethyl-N (XIV)	0.5	2.0	7.0	5.1	6.4	16.3	23.1	16.8	18.4	30.0	17.5	19.2	16.4	28.7	18.3	14.9	22.9	14.9	19.5
2,7-Dimethyl-N (XV)	...	...	...	...	...	...	...	...	...	0.3	...	0.3	0.5	...	0.3	1.5	2.9	2.7	3.9
1,2,3-Trimethyl-N (XVI)	...	Trace	1.2	Trace	0.1	3.1	1.8	3.4	5.2	1.9	3.0	4.5	5.4	1.4	2.0	3.0	2.5	2.1	1.8
1,2,4-Trimethyl-N (XVII)	...	1.2	3.5	Trace	2.0	4.2	8.2	6.3	5.0	12.1	6.5	6.8	7.0	11.0	5.8	4.8	8.4	3.6	4.5
1,2,7-Trimethyl-N (XVIII)	...	...	...	...	Trace	Trace	6.3	6.9	7.1	10.3	8.6	12.3	15.5	9.8	8.8	24.8	14.2	9.6	24.0
1,2,3,4-Tetramethyl-N (XIX)	...	Trace	0.3	...	0.1	0.9	1.4	3.9	5.1	4.8	4.3	7.5	2.9	5.9	2.6	2.1	3.5	1.8	1.1
x,x,x,x-Tetramethyl-N (XX)[f]	...	...	0.2	...	0.1	0.6	1.2	3.6	4.5	4.1	3.8	7.2	6.7	3.6	2.7	7.1	5.5	2.8	3.3
1,2,4,7-Tetramethyl-N (XXI)	...	0.1	1.0	...	0.2	2.4	7.1	6.5	7.2	12.5	8.7	12.3	12.2	13.0	6.7	16.4	11.7	4.9	15.7
1,2,3,4,6-Pentamethyl-N (XXII)	...	...	0.1	...	...	0.5	3.1	7.2	10.8	8.0	10.1	17.6	20.0	10.1	5.6	10.3	3.9	2.3	1.1
1,2,3,4,6,7-Hexamethyl-N (XXIII)	...	...	...	...	...	...	...	...	2.0	...	...	4.1	2.6	...	...	1.2	...	...	...
Heptamethyl-N (XXIV)[g]	...	...	...	...	...	...	...	...	...	...	...	Trace	3.8	...	...	Trace	...	...	...
Octamethyl-N (XXV)[g]	...	...	...	...	...	...	...	...	...	...	...	...	1.7	...	...	...	...	...	...
Perylene	...	...	...	...	...	...	...	...	...	...	...	...	...	0.8	0.7	1.0	4.0	3.7	4.8
Unidentified[h]	(0.3)	(0.3)	(0.2)	(1.5)	(1.2)	(1.0)	(3.9)	(3.8)	(2.6)	(8.7)	(15.0)	(3.3)	(1.3)	(5.0)	(26.0)	(6.9)	(2.5)	(29.5)	(2.6)
Depth of ring methylation[i]	0.8	1.0	1.5	1.0	1.2	1.7	2.3	2.7	3.0	2.9	3.0	3.5	3.7	3.3	2.8	3.3	2.6	2.2	2.4

[a] In each experiment (except no. 13) total amounts of starting materials used were 14.4 g (0.1 mol) of I and 32 g (1 mol) of methanol. In run 13 the amount of methanol used was increased to 64 g. [b] Calculated on the basis of 100 mol of starting I (including unreacted material). No quantitative analysis of the side products from methanol, *i.e.*, dimethyl ether, carbon monoxide, and hydrogen,[3] was undertaken. Qualitative tests with a solution of 2,4-dinitrophenylhydrazine showed the presence of small amounts of formaldehyde in the gaseous products above 420°. [c] N = naphthalene. [d] Mainly 2,4-dimethyl-1-naphthol (VIIa). [e] Tentative structure for a product which gave a vpc peak different from V but which was convertible into V by treatment with aqueous sodium hydroxide and then acid. [f] Tentative structure (as based on vpc retention volume and mechanistic considerations[22] only) for 1,2,6,7-tetramethylnaphthalene. [g] Tentative structure, as based on vpc data only. [h] Percentage by weight of total product. For experiments up to 420° these are mainly unidentified chromatographic peaks. Above 420° they are carbon deposits and non-distillable residues. [i] In average number of methyl groups per naphthalene or hydronaphthalene moiety for all identified products (exclusive of recovered I).

ring increases from *ca.* 1 (at 275°) to a maximum of 3–4 (at 420°) and then apparently decreases again. Preferential formation of specific polymethylnaphthalene isomers, particularly 1,2-di-, 1,2,4- and 1,2,7-tri-, 1,2,4,7-tetra-, and 1,2,3,4,6-pentamethyl compounds, occurs. At the same time lesser amounts of naphthalene, the two monomethylnaphthalenes, and the polymethylnaphthalenes with substituents in the 2,7, 1,2,3, 1,2,3,4, 1,2,6,7 (?), and 1,2,3,4,6,7 positions (as well as possible small amounts of hepta- and octamethyl compounds, from run 13 only) are formed. Comparison of this limited array of methylnaphthalenes obtained with the large number of theoretically possible isomers (10, 14, 32, 14, 10 for di, tri-, tetra-, penta-, and hexamethylnaphthalenes, respectively) clearly indicates that an oriented and selective pathway of methylation is involved.

The necessary presence of the arenolic group for effecting ring methylation of I was established by a separate series of experiments in which methanol solutions of 2-methyl-, 1,2-dimethyl-, and 1,2,4-trimethylnaphthalenes were subjected to the same conditions as employed in expt 16. No reaction was observed in any of these experiments. Recovery of starting materials was 92–95%. In another experiment, a portion of the total product mixture from expt 14 was dissolved in methanol (five parts by wt), and the solution was passed over catalyst A at 420°. No change in composition of the product mixture was found. These results also indicate that (at least up to 470°) a methylated naphthalene, once formed, does not isomerize, demethylate, or undergo intermolecular methyl group transfer. It also appears that the high degree of orientation selectivity in the ring-methylation process is ascribable to the influence of the arenolic group.

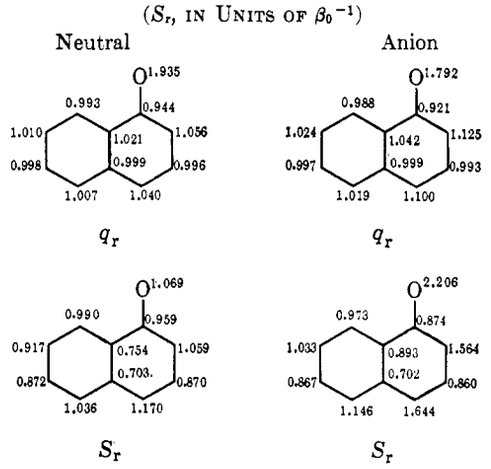
Discussion

It is well known[12] that arenols are more strongly adsorbed on chromatographic alumina than are the corresponding arenes or alkylarenes. With our catalyst the same relative adsorbabilities were found. Thus, the methylated naphthalenes were largely effused from the catalyst bed during the run proper, while residual amounts retained on the catalyst surface were easily desorbed by washing with benzene. On the other hand, unreacted I and its methyl derivatives (V–VII) remained to a large extent adsorbed on the benzene-washed catalyst, from which they could be removed by prolonged extraction with boiling acetone. By analogy with the alumina chemisorption of hydrogen chloride and ammonia the adsorption of I may be vizualized as occurring on acid–base (ion-pair) sites[13] with the proton attached to the basic site and the naphthoxy anion to an adjacent acidic site. Alternatively I may undergo nondissociative adsorption by means of the OH group with resultant weakening of the OH bond.[14] Orientation of the aromatic ring of I on the catalyst surface in the methylation reaction will be considered later.

In Scheme I are presented calculated reactivity indices (π-electron densities, q_r; superdelocalizabilities, S_r) for electrophilic attack at the various positions in I and in 1-naphthoxy anion. Data were obtained by use of simple Hückel molecular orbital theory and the parameters $\alpha_{O} = \alpha_0 + 2.0\beta_0$, $\beta_{C-O} = 0.8\beta_0$ for the neutral molecule[15] and $\alpha_{O} = \alpha_0 + \beta_0$, $\beta_{C-O} = \beta_0$ for the anion. No change in the orders of the indices was observed for small changes in the parameters. One sees that monomethylation should be more facile in the oxygen-bearing ring where attack would be preferred at the oxygen atom and at C-2 and C-4, especially if I is in the ionized form. Substitution into the second ring should be preferred at C-5 and C-7 in the anion, as well as, perhaps, at C-8 in the neutral molecule. Since these calculations do not take into account the entropies of activation for substitution at the various positions, it is to be expected that the data must be modified in order to be of suitably predictive value. Two major entropy factors can be readily visualized. These involve (1) *peri* effects[16] and (2) effects of orientation of the substrate with respect to the catalyst surface. Factor 1 may serve to diminish markedly substitution at C-8 due to the presence of the *peri* oxygen atom at C-1. On the other hand, factor 2 may serve to lower the entropy of activation particularly for substitution at C-2 (and possibly at C-8) if the naphthol molecule or anion were adsorbed in a vertical configuration.[17] If one assumes that the methylating agent is confined to the surface layer, then the observed methylations at C-4, C-6, and C-7 would seem to imply the adsorption of a significant percentage of molecules in a flatwise configuration.[17] On the other hand, the gross predominance of 2-methyl-1-naphthol over that of 4-methyl-1-naphthol at temperatures up to 350° contrasts with the closeness of calculated reactivity indices for the 2 and 4 positions and the known strongly preferential electrophilic attack at C-4 for most reactions occurring in solution.[18] Such preference for 2 substitution in the present reaction might be ascribed either to vertical

SCHEME I

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



(12) H. H. Strain, "Chromatographic Adsorption Analysis," Interscience Publishers, Inc., New York, N. Y., 1942, pp 14, 15, 92.

(13) J. B. Peri, *J. Phys. Chem.*, **69**, 231 (1965); **70**, 1482, 3168 (1966); B. D. Flockhart, C. Naccache, J. A. N. Scott, and R. C. Pink, *Chem. Commun.*, 238 (1965).

(14) J. R. Jain and C. N. Pillai, *Tetrahedron Lett.*, 675 (1965).

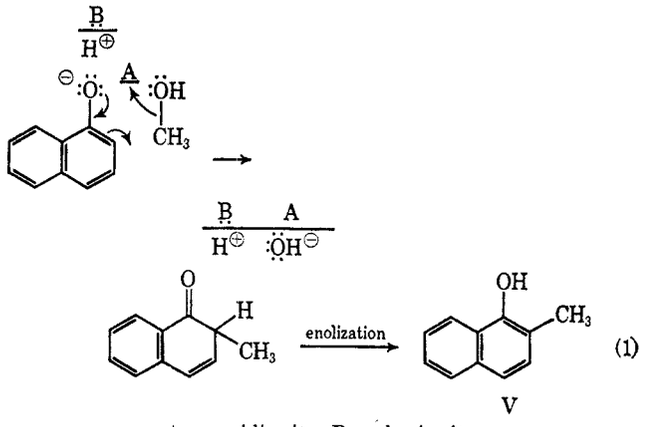
(15) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 117–135.

(16) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

(17) Compare C. H. Giles, T. H. MacEwan, S. N. Nakhwa, and D. Smith, *J. Chem. Soc.*, 3973 (1960), and L. R. Snyder, *J. Chromatog.*, **16**, 55 (1964), for varying geometries of chromatographic adsorption of phenol.

(18) L. F. Fieser and M. Fieser, "Introduction to Organic Chemistry," D. C. Heath, Boston, Mass., 1957, p 480.

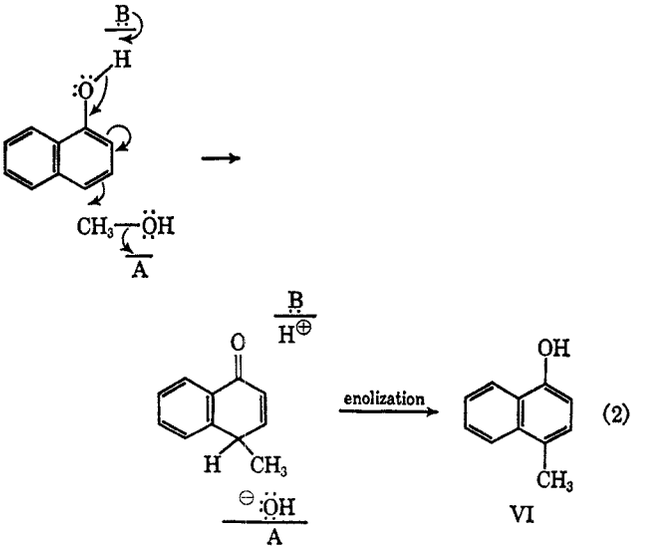
adsorption of I to a major extent or, alternatively, to the intervention of a cyclic transition state involving one molecule of flatwise-adsorbed naphthol, one molecule of methanol, and a single acidic site on the catalyst surface, as shown in eq 1. The latter mechanism for *ortho* methylation would seem to have much in common with the Claisen reaction of alkylating sodium phenoxide with an active halide,[19] the Tiffeneau rearrangement for *ortho* hydroxymethylation of a benzylmagnesium halide with formaldehyde,[19] and the aluminum phenoxide catalyzed *ortho* alkylation of phenols.[20]



(1)

A = acidic site; B = basic site

Although O-methylation of I might be expected to be faster than C-methylation, combined yields of 1-methoxynaphthalene and 1-methoxy-2-methylnaphthalene at 275–300° are much lower than those of 2-methyl-1-naphthol. This result may be due to the reversibility of the O-methylation reaction[5,21,22] and/or to extensive shielding by the catalyst surface of the oxygen atom from attack by the methylating agent. Ring methylation, on the other hand, is essentially irreversible under the same experimental conditions.[23] Although eq 1 has been written for a preliminary ionization step, it may be that the process of ionization is concerted with that of methylation. Either type of mechanism could also serve to give 4-methyl-1-naphthol if A were, instead, located in the proximity of C-4 as shown in eq 2.



(2)

Successive methylation at C-2 and C-4 would give 2,4-dimethyl-1-naphthol; while repeated methylation at either C-2 or C-4 would lead to 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene (IX) or to 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene (X), respectively. The roles of the oxygen-bearing compounds III, V, VI, VIIa, IX, and X as possible intermediates in the formation of methylnaphthalenes were studied separately under reaction conditions. The results and their mechanistic significance are presented in subsequent papers.[22,23] No naphthols or oxodihydronaphthalenes with methyl substituents in the unsubstituted ring of I were isolated. As indicated in later work,[23] however, such intermediates are presumed to be present in the reaction mixture above 300° but to have lifetimes which are too short to allow isolation by our procedure.

The exact nature of the methylating agent has not been established. In eq 1 and 2 adsorption of the methanol to an acidic site on the catalyst is shown as occurring through coordination of a nonbonding electron pair on the alcoholic oxygen.[14] Although it is also indicated that the methylation process is a concerted one, one cannot exclude the possibility of preliminary formation of a methyl carbonium ion. Inasmuch as methanol undergoes dehydrogenation to formaldehyde and carbon monoxide[3] during the reaction and the over-all process of converting a naphthol into a methylated naphthalene involves reduction, one might also consider that formaldehyde or hydroxymethyl carbonium ion ($^{\oplus}CH_2OH$) is the active electrophilic agent.[24] Although no hydroxymethyl compounds were isolated from our reaction mixtures, it is known that hydroxymethylbenzenes are readily converted into methylbenzenes over alumina at 400°.[21]

At 470–550° the reaction mixture contains a significant amount (3.7–4.8 mol per 100 mol of I used, *i.e.*, 7–10% yield) of perylene from condensation of two molecules of I. Also at these high temperatures appreciable carbonization occurs.

The reference compound 1,2,4,7-tetramethylnaphthalene (XXI) was synthesized by an unambiguous method. First Friedel–Crafts succinoylation of toluene[25,26] gave β-(4-methylbenzoyl)propionic acid, converted into its ethyl ester. The position of succinoylation was established by observation of the pmr spectra of these two products, each of which showed only an AB quartet at *ca.* δ 7.5 for the aromatic protons. The ester was then transformed into XXI in an over-all yield of 23% for six steps, one of which produced the known γ-(4-tolyl)valeric acid—free of *meta* isomer[27–29]

(19) C. C. Price, *Org. Reactions*, **3**, 1 (1946).

(20) R. Stroh, R. Seydel, and W. Hahn, "Newer Methods of Preparative Organic Chemistry," Vol. II, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1963, pp 337–359. See especially A. J. Kolka, J. P. Napolitano, A. H. Filbey, and G. G. Ecke, *J. Org. Chem.*, **22**, 642 (1957).

(21) E. I. Heiba and P. S. Landis, *J. Catal.*, **3**, 471 (1964).

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

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

(24) R. C. Greenler, *J. Chem. Phys.*, **37**, 2094 (1962). We are investigating such possibilities at the present time.

(25) E. B. Barnett and F. G. Sanders, *J. Chem. Soc.*, 434 (1933).

(26) S. Dev, *J. Indian Chem. Soc.*, **25**, 315 (1948).

(27) (a) Our efforts to prepare this acid by Friedel-Crafts reaction of γ-valerolactone with toluene either according to the procedure of Phillips[24] or to that of Chaudhuri[24] gave a mixture of *meta* and *para* isomers as determined by pmr analysis. (b) Cyclization of the mixed saturated isomeric acids[28] gave both XXIX and 1-oxo-4,6-dimethyl-1,2,3,4-tetrahydronaphthalene, separable by vpc. The pmr spectrum of the latter ketone differs from that of XXIX principally in the aromatic region where it shows two overlapping signals at δ 6.8–7.2 for protons at C-5 and C-7 and a doublet (δ 7.82, J = 8 cps) for the proton at C-8.

(28) D. D. Phillips, *J. Amer. Chem. Soc.*, **77**, 3658 (1955).

(29) N. Chaudhuri, *Sci. Cult.* (Calcutta), **18**, 442 (1953).

TABLE II

COMPARATIVE PROPERTIES OF METHYL-SUBSTITUTED NAPHTHALENES ISOLATED FROM REACTION MIXTURES

Position(s) of methyl substituent(s)	Expt no.[a]	r_V[b]	Mp, °C		Picrate mp, °C		Styphnate mp, °C	
			Found	Lit.[c]	Found	Lit.[c]	Found	Lit.[c]
None[d]	14, 19	1.00	80–80.5	80.2	...	...	...	...
1[d]	8–19	1.77	Liquid	−30.8	...	...	...	...
2[d]	8–19	1.65	34–35	34.4	115–117	116–117	...	...
1,2[d]	6–10	3.08	Liquid	−1.6	130–132	131	142–143.5	143.5
1,2,3[e]	12, 13	4.74	27.5–28	27–28	142.5–143	142.5	...	...
1,2,4[d]	10, 16	4.52	54–55	54–55	147–148	148	123–124	123.5
1,2,7[d]	10, 16	3.85	Liquid	13[f]	129–131	129–131	158–159	159
1,2,3,4[e]	12, 14	8.89	107–107.5	107	182–183	182–183	...	...
1,2,4,7[d,g]	16	6.95	46–47	...	146–147	...	...	...
1,2,3,4,6[e]	13, 16	12.70	85–86	85	175–176	176	...	...
1,2,3,4,6,7[e]	12, 16	20.60	143–145	145	190–191	190.5	...	...

[a] Experiments from which methyl-substituted naphthalenes were isolated. [b] Retention volume, relative to naphthalene as internal standard, on a Bentone–Apiezon column (see text); helium flow rate, 85 cc/min; temperature, 170° for mono- and dimethylnaphthalenes and 200° for all others. [c] Unless otherwise indicated, data are from ref 31a. [d] Identified by direct comparison with an authentic sample. [e] Structure assigned on the basis of the physical properties given as well as of infrared and pmr spectra. [f] See ref 32. [g] See ref 30.

(see Experimental Section). The pmr and infrared spectra were in agreement with the assigned structure of 1,2,4,7-tetramethylnaphthalene (*vide infra*). The physical properties of our hydrocarbon, however, were different from those reported by Colonge and Grimaud for a product (derived from initial Friedel–Crafts alkylation of toluene by means of ethyl 2-methyl-2-penten-1-oate) to which they ascribe structure XXI without adequate proof.[30]

Experimental Section

Apparatus, Catalysts, and Procedure.—Reactions were carried out in a flow system consisting essentially of a vertically mounted 75 cm × 1.6 cm (i.d.) stainless steel tube, provided at the top with a constant-rate dropping funnel and connected at the outlet to a series of coolers and traps. The reactor tube was heated with a furnace (60 cm in length), equipped with three separately controlled heating coils, which by proper adjustment provided an isothermal zone 45 ± 3 cm in length. The temperature of this zone was measured to an estimated accuracy of ±3°.

In each run there was employed 80 g of fresh alumina catalyst in the form of a bed 40 cm long and situated in the isothermal zone. Catalyst A was prepared[9] by hydrolysis of freshly distilled aluminum isopropoxide with excess distilled water at 85–95°. The precipitate was washed thoroughly with distilled water, filtered, dried at 120° for 36 hr, powdered, and compressed in the form of 1/8-in. pellets. Catalyst B (Harshaw Chemical Co., Cleveland, Ohio, Grade AL-0104 alumina, 1/8-in. pellets) and catalyst C (Houdry Process Corp., Philadelphia, Pa., hard alumina, Grade HA-100, cylindrically extruded 1/8-in. pellets) were obtained commercially.

The catalyst bed was activated *in situ* before each experiment by heating at 650° for 16 hr in a stream of dry nitrogen. The desired reaction temperature was then established and absolute methanol (60–70 ml) was passed over the catalyst for 30–35 min. This was followed by the dropwise addition of a mixture of the reactants, *viz.* 1-naphthol (14.4 g, 0.1 mol) and absolute methanol (32 g, 1 mol), over a period of 2 hr. Finally, an additional portion of methanol (10 ml) was passed through the reactor. A constant flow of nitrogen (22 cc/min) was maintained throughout the experiment. In most cases liquid product started to appear in the first, water-cooled trap only after the lapse of 20–25 min. At the end of the reaction the catalyst was washed with benzene (50 ml) to elute remaining methylnaphthalenes, and was then removed from the tube and treated with boiling acetone to complete extraction of the more strongly adsorbed naphthols. Combined condensates and extracts were evaporated to remove solvents. The organic product was separated from a water layer, dissolved in ether, and washed with 10% aqueous sodium hydroxide and then with water. The alkaline extract was acidified with hydrochloric acid and extracted with ether. Evaporation of the ether solutions gave a neutral fraction and an acidic one.

For the neutral products from expt 1–9 separation of components was effected on an 8 ft × 3/8-in. (o.d.) column packed with 60–80 mesh acid-washed Chromosorb P impregnated with 10% Bentone-34 and 5% Apiezon L. The carrier gas was helium. The column temperature was 170° for oxohydronaphthalenes, naphthalene, and mono-, di-, and trimethylnaphthalenes and 200° for polymethylnaphthalenes. For acidic products separation was conducted through the combined use of two columns, one (6 ft × 0.25-in.) packed with 10% Apiezon L on Chromosorb P and the other (5 ft × 3/8-in.) packed with 10% Carbowax 20M on the same support. In expt 10–19 the neutral fraction was first distilled at 0.5 mm. The distillate (bp ≤160°) was then examined by vpc as before. The same columns were used for quantitative analysis of the reaction mixtures.

The distillation residues from runs 14–19 were subjected to liquid–solid chromatography on a column (40 cm × 3.2 cm) of Alcoa F-20 alumina by means of cyclohexane and then benzene–cyclohexane (1:1 v/v) as eluents. Total weights of eluted products were determined (see footnote *i*, Table I), but these compounds were not analyzed further. A yellow zone with a strong greenish fluorescence was separated from the column and extracted with hot chloroform. Evaporation of the extract and recrystallization of the residue from ethanol–chloroform gave perylene, yield determined by direct weight.

Data on the analytical results for the various runs are presented in Table I. The estimated absolute error in vpc percentages, as based on repeated analyses of the same product mixture and of synthetic mixtures, is ±0–0.7% for each component. The reproducibility of results, as determined by repeating experiments under identical reaction conditions, is ±0–1.5% (absolute) for each component.

Identification of Individual Components.—Hydrocarbons XI–XIV, XVII, XVIII, XXI, and perylene (mp 272–274°, lit.[31b] 273–274°) were identified by direct comparison (in various combinations of melting point, mixture melting point, relative retention volume (r_V) in vpc, infrared, and pmr spectra) with authentic reference samples and their derivatives (*cf.* Tables II and III). It might be noted that 1,2,4- and 1,2,7-trimethylnaphthalenes (XVII and XVIII) show three different signals of equal areas for methyl protons in their pmr spectra. The reference compounds in these cases were synthesized from purified samples of 1,4- and 2,7-dimethylnaphthalenes, respectively, by successive steps of chloromethylation and reduction.[32] If the third methyl group actually occupied any ring position other than C-2 or C-1, respectively, only two different methyl proton

(30) J. Colonge and E. Grimaud [*Compt. Rend.*, **231**, 580 (1950); *Bull. Soc. Chim. Fr.*, 857 (1951)] synthesized a hydrocarbon of mp −3° (picrate mp 151°, styphnate mp 118°), to which they assigned the structure of 1,2,4,7-tetramethylnaphthalene. This assignment was based on the unproved assumption that Friedel–Crafts alkylation of toluene by means of ethyl 2-methyl-4-penten-1-oate gives ethyl 2-methyl-4-(4-tolyl)pentanoate. It seems likely that these authors synthesized, instead, either an isomeric tetramethylnaphthalene or a mixture of isomers (*cf.* ref 27a).

(31) E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIIB, Elsevier Publishing Co., Amsterdam, 1956, (a) pp 1286–1288, (b) p 1505.

(32) W. Ried and H. Bodem, *Chem. Ber.*, **91**, 1354 (1958).

TABLE III

PROTON MAGNETIC RESONANCE CHARACTERISTICS OF SOME METHYL-SUBSTITUTED NAPHTHALENES[a]

Positions of methyl groups	Methyl protons: δ, ppm;[b] relative areas	Aromatic protons: δ, ppm (multiplicity); J, cps, assignment; relative areas
1,2 (XIV)	2.33, 2.41;[c] 0.9:1	6.9–8.0 m
1,2,3 (XVI)	2.31, 2.39, 2.54; *ca.* 1:1:1	7.2–8.0 m
1,2,4 (XVII)	2.31, 2.41, 2.51; *ca.* 1:1:1	6.94 s, H-3; 7.1–7.6 m, β protons at C-6 and C-7; 7.6–8.0 m, α protons at C-5 and C-8; *ca.* 1:2:2
1,2,7 (XVIII)	2.25, 2.32, 2.38; *ca.* 1:1:1	6.8–7.7 m
1,2,3,4 (XIX)	2.31; 2.51; 1:1	Symmetric A_2B_2 system centered at 7.59; 7.1–7.5 m, β protons at C-6 and C-7; 7.7–8.1 m, α protons at C-5 and C-8; 1:1
1,2,4,7 (XXI)[d]	2.20, 2.30, 2.41; 1:1:2	6.79 s, H-3; 7.01 (doublet of doublets) J = 8.5 and J = 1.5, H-6; 7.4–7.7 m,[e] H-5 and H-8; 1:1:1.9
1,2,3,4,6 (XXII)	2.31, 2.48, 2.50; *ca.* 2:1:2[f]	7.10 (doublet of doublets) J = 8.8 and J = 2.0, H-7; 7.5–7.9 m,[g] H-5 and H-8; 1:2
1,2,3,4,6,7 (XXIII)	2.36, 2.42, 2.55; *ca.* 1:1:1	7.65 s, α protons at C-5 and C-8

[a] Solvent, CCl_4. Relative areas of methyl aromatic protons are in good agreement with assigned structures. [b] All appear to be singlets, but overlapping is extensive in some cases. [c] I. C. Lewis [*J. Phys. Chem.*, **70**, 1667 (1966)] reports methyl proton signals at 2.47 and 2.57 for this compound in the same solvent. [d] Marked changes occur in this spectrum (others not investigated) on changing the solvent to $CDCl_3$; observed data, δ 2.37, 2.49, 2.54—areas 1 : 2 : 1; plus entire aromatic region shifted downfield by *ca.* 20 cps. The change in relative areas of the three methyl proton signals is consistent with the presence in the molecule of four magnetically distinguishable methyl groups. [e] This region consists of a doublet at δ 7.60 ($J \simeq 8$ cps) for the proton at C-5 and a superimposed singlet at δ 7.57 for that at C-8. [f] The ratio of areas for the signals at 2.48 and 2.50 is based on visual observation of the spectrum. [g] This region consists of a doublet at δ 7.77 ($J \simeq 9$ cps) for the proton at C-8 and an adjacent broadened singlet at δ *ca.* 7.63 for that at C-5.

signals should be observed.[33] 2,7-Dimethylnaphthalene (XV) was not isolated but was identified only by r_V (direct comparison with authentic samples of all possible dimethylnaphthalenes).

1,2,3-Tri- (XVI), 1,2,3,4-tetra- (XIX), 1,2,3,4,6-penta- (XXII), and 1,2,3,4,6,7-hexamethylnaphthalenes (XXIII) were identified by pmr and infrared spectra and by comparison of melting points of the hydrocarbons and their picrates with literature values. The pmr spectrum of XIX clearly shows an A_2B_2 pattern for protons in the unsubstituted ring and two singlets (of equal areas) for two sets of equivalent methyl groups. The infrared spectrum in the 1650–2000-cm^{-1} region (measured in CS_2) shows a typical pattern for an *ortho*-disubstituted benzene ring,[34] *i.e.*, singlets at 1693 and 1740 cm^{-1}, a doublet at 1793 and 1818 cm^{-1}, and a triplet at 1887, 1912, and 1939 cm^{-1}. The infrared spectrum of XVI shows the same pattern (1686, 1743, 1786, 1811, 1890, 1910, and 1937 cm^{-1}) plus one other band (1713 cm^{-1}), possibly owing to the lone hydrogen in the methyl-substituted ring. XXII shows (intensities: s = strong, m = medium, w = weak) $\nu_{max}^{CS_2}$ 769 m cm^{-1}, 810 s, 872 s, 1045 m, 1187 m, 2930 s; $\nu_{max}^{CHCl_3}$ 1384 s cm^{-1}, 1452 s, 1517 s, 1595 m, 1629 m, 1721 w, 1760 w, 1907 w. XXIII has $\nu_{max}^{CS_2}$ 865 s cm^{-1}, 1003 m, 2930 s, 2950 s; $\nu_{max}^{CHCl_3}$ 1378 s cm^{-1}, 1447 s, 1502 m, 1590 m, 1705 m, 1772 w.

The pmr spectrum of XXII shows features characteristic of the presence of two aromatic protons in a vicinal α,β arrangement on the ring and of one other aromatic proton in an α position. Only three isomeric structures, 1,2,3,4,6-, 1,2,3,5,6-, and 2,3,4,-5,6-pentamethylnaphthalenes, are consistent with this spectral evidence. The presence of strong CH out-of-plane deformation bands at 810 (for two adjacent free hydrogen atoms) and 872 cm^{-1} (lone aromatic hydrogen)[35] in the infrared spectrum corroborates these possible assignments. A final choice was made on the basis of the pattern of absorption bands (1721, 1760, and 1907 cm^{-1}) in the 1650–2000-cm^{-1} region which is consistent with the presence of all of the aromatic hydrogen atoms in one ring (1,2,4-trisubstituted benzene) as occurs in the 1,2,3,4,6 isomer, but is inconsistent with the presence of two aromatic hydrogen atoms in one ring and one in the other (*i.e.*, for superposition of bands from a pentasubstituted benzene and a 1,2,3,4-tetrasubstituted benzene) as occur in the other two possible isomers. The pmr spectrum of XXIII shows features of three equally intense methyl proton signals and a singlet for two unoccupied α positions in the ring. Again three isomeric structures, 1,2,3,4,6,7-, 1,2,3,5,6,7-, and 2,3,4,5,6,7-hexamethylnaphthalenes, are consistent with this evidence. The infrared spectral pattern for XXIII (medium band at 1705 and a much weaker band at 1772 cm^{-1}) is typical of a 1,2,4,5-tetrasubstituted benzene ring (as occurs in the 1,2,3,4,6,7 isomer), but is inconsistent with the presence of a pentasubstituted ring (as occurs in each of the other possible isomers). Corroborating the assignment is also the presence of a single strong band (at 865 cm^{-1}) for a lone aromatic hydrogen. One might also note that bands at 870 and 881 cm^{-1} in the infrared spectrum of XXI are apparently due to the lone hydrogens at C-3 and C-8, while a strong band at 810 cm^{-1} can be assigned to the two adjacent hydrogens at C-5 and C-6.

The tentative assignment of the last two peaks in the chromatogram from expt 13 to hepta- and octamethylnaphthalenes is based on a comparison of retention volumes of compounds XII–XXIII on a silicone rubber column with their reported boiling points and extrapolation of the results to those of the two higher components. The unidentified components were found to have proper boiling ranges for the assigned structures, *i.e.*, 350 ± 10 and 365 ± 10° (760 mm), respectively.

1-Methoxynaphthalene was isolated from expt 4: r_V = 5.1 at 170° (see Table III, footnote *b*); pmr spectrum: singlet, 3 H (δ 3.86) methoxy group; multiplet, 7 H (6.5–8.3) aromatic protons; identical in infrared spectrum and r_V with an authentic sample. 1-Methoxy-2-methylnaphthalene was isolated from expt 4: pmr spectrum: singlet, 3 H (δ 2.40) aromatic methyl group; singlet, 3 H (3.84) methoxy group; multiplet, 6 H (7.0–8.2) aromatic protons; ν_{max}^{neat} 1247 (Ar–O stretch) and 1092 cm^{-1} (Me–O).[36] Some of this ether was refluxed with pyridine hydrochloride[37] to give 2-methyl-1-naphthol. 2-Methyl-1-naphthol was isolated from expt 5: mp 63.5–64° (lit.[38] 63–64°); $\nu_{max}^{CS_2}$ 3620 cm^{-1} (OH); pmr spectrum (in CS_2): singlet (δ 2.17) methyl group, singlet (5.02) OH, and multiplet (6.9–8.1) aromatic protons; identical with a synthetic sample. 4-Methyl-1-naphthol was isolated from expt 3 and 5: mp 83–85° (lit.[37] 85°); pmr spectrum (in $CDCl_3$): slightly split singlet, 3 H (δ 2.56, J = 1 cps) methyl group; singlet, 1 H (5.42) OH; AB quartet centered at δ 6.84, 2 H ($\Delta\delta_{AB}$ = 26 cps, J_{AB} = 7.5 cps)[39] but with apparent long-range splitting ($J \simeq 1$ cps) in the downfield half—probably protons at C-2 and C-3; multiplet, 2 H (7.3–7.7) probably protons at C-6 and C-7; multiplet, 2 H (7.7–8.4) probably protons at C-5 and C-8; identical with a synthetic sample. 2,4-Dimethyl-1-naphthol was isolated from expt 3 and 5: mp 81–83° (lit.[37] 82–83°); pmr spectrum: two singlets, 3 H each (δ 2.22, 2.51) methyl groups; singlet, 1 H (4.80) OH; singlet, 1 H (6.93) proton at C-3; multiplet, 4 H

(33) *Cf.* C. MacLean and E. L. Mackor, *Mol. Phys.*, **3**, 223 (1960).

(34) C. W. Young, R. B. DuVall, and N. Wright, *Anal. Chem.*, **23**, 709 (1951); D. H. Whiffen, *Spectrochim. Acta*, **7**, 253 (1955).

(35) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964, pp 231, 232; J. G. Hawkins, E. R. Ward, and D. H. Whiffen, *Spectrochim. Acta*, **10**, 105 (1957).

(36) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co. Ltd., London, 1958, pp 115–117.

(37) N. P. Buû-Hoi and D. Lavit, *J. Chem. Soc.*, 2776 (1955).

(38) M. Tishler, L. F. Fieser, and N. L. Wendler, *J. Amer. Chem. Soc.*, **62**, 2866 (1940).

(39) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, pp 89, 90.

(7.2–8.2) aromatic protons at C-5 to C-8; identical with a synthetic sample.

1-Oxo-2,2-dimethyl-1,2-dihydronaphthalene (IX) was isolated from expt 6: pmr spectrum: singlet, 6 H (δ 1.24) methyl groups; AB quartet centered at δ 6.25, 2 H ($\Delta\delta_{AB}$ = 17 cps, J = 9.5 cps)[39] protons at C-3 and C-4; multiplet, 3 H (7.0–7.7) protons at C-5, C-6, and C-7; multiplet, 1 H (7.8–8.2) proton at C-8; ν_{max}^{neat} 690 m cm^{-1}, 790 s, 890 m, 994 m, 1305 m, 1468 m, 1600 m, 1684 s, 2880 m; r_V = 2.4 at 170°; identical with a synthetic sample. It might be noted that the CH out-of-plane deformation frequency (at 790 cm^{-1}) for the four adjacent aromatic hydrogens is considerably higher than that of *o*-xylene (742)[40a] or of 1,2,3,4-tetrahydronaphthalene (742).[40b] This may result from the combined conjugation effects of the carbonyl group and the double bond in IX. A weaker shift in the same direction was found for *o*-methylstyrene (772).[41]

1-Oxo-4,4-dimethyl-1,4-dihydronaphthalene (X) was isolated from expt 3 and 6: mp 70–71° (lit.[42] 69.5–70.5°); pmr spectrum: singlet, 6 H (δ 1.43) methyl groups; AB quartet centered at δ 6.55, 2 H ($\Delta\delta_{AB}$ = 33 cps, J_{AB} = 10 cps)[39] protons at C-2 and C-3; multiplet, 3 H (7.0–7.6) protons at C-5 to C-7; multiplet, 1 H (7.8–8.2) proton at C-8; $\nu_{max}^{CS_2}$ 770 s, cm^{-1}, 843 s, 1039 m, 1093 m, 1158 s, 1309 s, 1379 m, 1401 m, 1471 s, 1484 m, 1604 s, 1665 s, 2985 s, 3033 m; r_V = 4.1 at 170°; identical with a synthetic sample. The CH out-of-plane deformation frequency (at 770 cm^{-1}) for four adjacent hydrogens falls between that of IX and that of *o*-xylene.

Analytical Methods.—Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill. Pmr spectra were obtained by means of a Varian Associates A-60 spectrometer. Tetramethylsilane was used as an internal reference and, unless otherwise noted, carbon tetrachloride was used as a solvent. Infrared spectra were obtained by means of a Beckman IR-7 spectrophotometer. Solutions in CS_2 or $CHCl_3$ (6–10% by wt) were examined in a cell of 0.1-mm thickness and pure liquids were examined directly between NaCl plates.

Source and Synthesis of Reference Compounds. A. Oxygen-Containing Compounds.—2-Methyl-1-naphthol[43,44] and 1-oxo-4,4-dimethyl-1,4-dihydronaphthalene[42] were prepared by reported procedures. 1-Methoxynaphthalene (Distillation Products) was purified by distillation *in vacuo*. It was converted into 4-methoxy-1-naphthaldehyde[37] [pmr spectrum: singlet (δ 3.67) methoxy group; AB quartet centered at δ *ca.* 6.85 ($\Delta\delta_{AB} \simeq$ 64 cps, J_{AB} = 7.5 cps)[39] probably protons at C-2 and C-3, but with the downfield half overlapping a multiplet (7.1–7.7), probably protons at C-6 and C-7; multiplets (7.8–8.2 and 9.1–9.4) probably protons at C-5 and C-8; singlet (9.97) aldehyde group] which was reduced to 1-methoxy-4-methyl-naphthalene[37] [pmr spectrum: slightly split singlet, 3 H (δ 2.46, J = 0.8 cps) aromatic methyl group; singlet 3 H (3.64) methoxy group; AB quartet centered at δ 6.65, 2 H ($\Delta\delta_{AB}$ = 35 cps, J_{AB} = 7.5 cps)[39] but with apparent long-range splitting (J = 0.8 cps) in the downfield half—probably protons at C-2 and C-3; multiplet, 2 H (7.1–7.5) probably protons at C-6 and C-7; multiplet with secondary splitting (J = 0.8 cps) 1 H (7.5–7.9) and multiplet 1 H (8.1–8.5) probably protons at C-5 and C-8]. Demethylation of this ether[37] gave 4-methyl-1-naphthol (VI).

To a stirred, ice-cold solution of 109.5 g (0.64 mol) of 1-methoxy-4-methylnaphthalene in 350 ml of methylene chloride was added 261 g of anhydrous stannic chloride and then (dropwise) 110 g (0.7 mol) of dichloromethyl *n*-butyl ether.[45] The stirred solution was allowed to attain room temperature and then was poured onto ice. The organic phase (plus extracts of the aqueous phase with the same solvent) was washed successively with 5% aqueous sodium bicarbonate solution and water, dried, and evaporated: yield 112 g (88%) of 1-methoxy-4-methyl-2-naphthaldehyde; mp 88–90° (after crystallization from ethanol); pmr spectrum, singlet, 3 H (δ 2.60) methyl group; singlet, 3 H (4.05) methoxy group; multiplet, 5 H (7.3–8.3) aromatic protons; singlet, 1 H (10.42) aldehyde group; lit.[37] mp 90°.

According to published directions[37] the immediately foregoing aldehyde was converted first into 1-methoxy-2,4-dimethylnaphthalene [pmr spectrum: singlet (δ 2.25) probably methyl at C-2; slightly split singlet (2.41, $J \simeq$ 1 cps) probably methyl at C-4; singlet (3.66) methoxy group; singlet (6.82) proton at C-3; multiplet (7.0–8.3) aromatic protons in unsubstituted ring] and then into 2,4-dimethyl-1-naphthol.

1-Oxo-2,2-dimethyl-1,2,3,4-tetrahydronaphthalene.—To a cold (10–15°), stirred mixture of 24.6 g (0.17 mol) of 1-tetralone (Aldrich Chemical Co.), 59.5 g (0.42 mol) of methyl iodide, and 100 ml of benzene in an atmosphere of nitrogen was added in portions over a period of 30 min a mineral oil dispersion of sodium hydride (6.7 g, 0.28 mol). The mixture was stirred at 55–60° for 5 hr, refluxed for 1 hr, stirred at room temperature overnight, and then poured into excess methanol. The residue from evaporation of solvents was extracted with ether. The ether extract was washed successively with water, 10% aqueous sodium carbonate solution, and water and then distilled: yield 21 g (71%); bp 88–89° (1 mm); n^{24}D 1.5395 [lit.[46] bp 124–126° (11 mm); n^{25}D 1.5388]; $\nu_{max}^{CCl_4}$ at 1690 cm^{-1} (strong, C=O); pmr spectrum: singlet, 6 H (δ 1.12), methyl group; two triplets, 4 H (1.84 and 2.87, J = 6 cps) dimethylene group; multiplet, 3 H (6.9–7.5) aromatic protons at C-5, C-6, and C-7; multiplet, 1 H (7.8–8.2) proton at C-8. These spectra were identical with those of an authentic sample made by a different method.[46]

1-Oxo-2,2-dimethyl-1,2-dihydronaphthalene (IX).—A mixture of 15.1 g (0.087 mol) of the preceding ketone, 19.6 g (0.11 mol) of N-bromosuccinimide, 58 ml of carbon tetrachloride, and 0.2 g of benzoyl peroxide was refluxed in an atmosphere of nitrogen for 5 hr. The cooled mixture was filtered to remove precipitated succinimide and evaporated to remove solvent. The residue was refluxed with 150 ml of 10% ethanolic potassium hydroxide for 45 min and the solvent was again evaporated. This residue was treated with water and extracted with ether. Distillation gave 9.8 g (65%) of IX, bp 72–74° (0.4 mm), n^{25}D 1.5725 (lit.[46] n^{24}D 1.5705).

B. Hydrocarbons.—Perylene was commercially available (Aldrich Chemical Co.). Purified samples of naphthalene, all mono- and dimethylnaphthalenes, and four trimethylnaphthalenes, were available from previous studies.[47] Reported procedures were followed for the syntheses of 1,2,4- and 1,2,7-trimethylnaphthalenes.[32] 1,2,4,7-Tetramethylnaphthalene was synthesized by the following series of steps.

4-(4-Tolyl)-3-penten-1-oic Acid (XXVII).—β-(4-Methylbenzoyl)-propionic acid[25,26] [pmr spectrum, singlet (δ 2.39) methyl group, symmetric A_2B_2 multiplet centered at δ 3.02 ($\Delta\delta_{AB}$ = 29 cps, $J_{AB}/\Delta\delta_{AB} \simeq$ 0.2)[48] dimethylene group, a slightly altered AB quartet centered at δ 7.58 ($\Delta\delta_{AB}$ = 38 cps, J_{AB} = 8 cps)[39] aromatic protons, singlet (11.06) carboxylic acid] was converted into ethyl β-(4-methylbenzoyl)propionate, mp 42–44° (lit. 42–43.5°), by a reported procedure:[26] $\nu_{max}^{CCl_4}$ 1735 (ester) and 1795 cm^{-1} (ketonic C=O); pmr spectrum, triplet (δ 1.19, J = 7 cps) methyl moiety of ester group, singlet (2.32) aromatic methyl group, symmetric A_2B_2 multiplet centered at δ 2.87 ($\Delta\delta_{AB}$ = 31 cps, $J_{AB}/\Delta\delta_{AB} \simeq$ 0.2)[48] dimethylene group, quartet (δ 4.07, J = 7 cps) methylene moiety of ester group, and an AB quartet centered at δ 7.49 ($\Delta\delta_{AB}$ = 38 cps, J_{AB} = 8 cps)[39] aromatic protons.

To a rapidly stirred cold (0°) solution of 30 g of this ester in a mixture of 100 ml of dry benzene and 100 ml of anhydrous ether was added dropwise a 1 molar equiv of methylmagnesium iodide in ether. After removal of most of the ether by distillation, the remaining mixture was refluxed for 1 hr by itself and then further with added dilute sulfuric acid. Extraction of the organic layer with excess aqueous sodium hydroxide and acidification of the aqueous extract yielded 17.6 g (63%) of crude unsaturated acids, presumably a mixture of 4-(4-tolyl)-4-penten-1-oic acid (XXVI) and XXVII: $\nu_{max}^{CS_2}$ 810, 828 (2 vicinal aromatic H, trisubstituted ethylene), 901 (C=CH$_2$), and 1720 cm^{-1} (C=O). The pmr spectrum (*vide infra*) indicated the presence of *ca.* 25–30% XXVI and 70–75% XXVII therein.

A sample of the mixed unsaturated acids in absolute ethanol was hydrogenated at 1 atm pressure by use of prereduced Adams platinum catalyst until the original faster rate of reaction due to the presence of XXVI[49] had terminated. The partially saturated mixture of acids was crystallized from carbon tetrachloride

(40) American Petroleum Institute, Research Project 44, "Infrared Spectral Data," Spectra No. (a) 310, (b) 463 and 1422.

(41) H. Pines and J. Shabtai, *J. Org. Chem.*, **26**, 4220 (1961).

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

(43) M. F. Hawthorne, *J. Org. Chem.*, **22**, 1001 (1957).

(44) T. L. Yarboro and C. Karr, *ibid.*, **24**, 1141 (1959).

(45) A. Rieche, H. Gross, and E. Höft, *Chem. Ber.*, **93**, 88 (1960).

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

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

(48) H. Suhr, "Anwendungen der kernmagnetischen Resonanz in der organischen Chemie," Springer-Verlag, Berlin, 1965, pp 67, 68.

(49) See, for example, L. H. Klemm and R. Mann, *J. Org. Chem.*, **29**, 900 (1964).

to give prisms of XXVII: mp 83–85°; $\nu_{max}^{CS_2}$ 808 and 1715 cm^{-1}; pmr spectrum: singlet, 3 H (δ 1.95) vinylic methyl group; singlet, 3 H (2.25) aromatic methyl group; doublet, 2 H (3.16, J = 7 cps) methylene group; triplet, 1 H (5.85, J = 7 cps) vinylic proton; distorted AB spectrum, 4 H (6.8–7.4) aromatic protons; singlet, 1 H (12.25) carboxylic acid group. Small splittings (*ca.* 1 cps) were observable in all pmr signals except that at δ 2.25 and possibly those in the aromatic region.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.96; H, 7.49.

By difference, the pmr spectrum of XXVI (as ascertained from the mixed acids) is found to be a singlet (δ 2.25) aromatic methyl group which presumably overlaps the upfield half of an A_2B_2 multiplet centered at *ca.* δ 2.4 for the dimethylene group, doublet (5.10, J = 15 cps) vinylic methylene group, multiplet (6.8–7.4) aromatic protons, and singlet (12.4) carboxylic acid group.

1-Oxo-2,2,4,7-tetramethyl-1,2,3,4-tetrahydronaphthalene (XXX).—Hydrogenation of 14 g of preceding mixed unsaturated acids until nearly an equimolar quantity of hydrogen had been absorbed gave 13 g (92%) of γ-(4-tolyl)valeric acid[27a] (XXVIII): $\nu_{max}^{CS_2}$ 807 (two vicinal aromatic H) and 1710 cm^{-1} (C=O); pmr spectrum, doublet (δ 1.22, J = 7 cps) aliphatic methyl group, singlet (2.25) aromatic methyl group superimposed on multiplet (1.5–2.9) for other aliphatic protons, singlet (6.97) aromatic protons, singlet (11.74) carboxylic acid group. This saturated acid was cyclized to 1-oxo-4,7-dimethyl-1,2,3,4-tetrahydronaphthalene (XXIX) by the method of Phillips:[28] $\nu_{max}^{CS_2}$ 815 and 825 (aromatic C–H) and 1690 cm^{-1} (C=O); pmr spectrum: doublet, 3 H (δ 1.30, J = 7 cps) methyl group at C-4; singlet (2.26) methyl group at C-7, superimposed on complex absorption at δ 1.5–3.2—total 8–9 H; singlet, 2 H (7.09) protons at C-5 and C-6; singlet (7.64) proton at C-8.[27b]

To a cold (10°), stirred mixture of 8.5 g (0.049 mol) of ketone XXIX, 7.5 ml (0.12 mol) of methyl iodide, and 29 ml of benzene in an atmosphere of nitrogen was added a mineral oil dispersion of sodium hydride (7.2 g, 0.3 mol). The mixture was stirred and refluxed for 7 hr, whereupon the theoretical amount of hydrogen had been evolved. The reaction mixture was poured into excess methanol. The residue from evaporation of the solvents was extracted with ether. The dried ether solution was distilled to give 8 g (81%) of XXX: bp 86–89° (0.15 mm); $\nu_{max}^{CS_2}$ 820 (aromatic C–H) and 1685 cm^{-1} (C=O); pmr spectrum: two singlets, *ca.* 6 H (δ 1.08, 1.16) *gem*-methyl groups at C-2; doublet, *ca.* 3 H (1.29, J = 7 cps) methyl group at C-4; singlet, *ca.* 3 H (2.26) methyl group at C-7, superimposed on complex multiplet *ca.* 3 H (1.5–3.3) for ring protons at C-3 and C-4; pseudo-doublet, 2 H (7.13, 7.16) protons at C-5 and C-6; singlet, 1 H (7.72) proton at C-8.

An analytical sample was obtained as a light yellow liquid, bp 88–89° (0.1 mm), n^{23}D 1.5250.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.21; H, 9.08.

1-Hydroxy-2,2,4,7-tetramethyl-1,2,3,4-tetrahydronaphthalene (XXXI).—To a stirred solution of 1 g of sodium borohydride in 20 ml of absolute ethanol was added, dropwise, 6 g of ketone XXX. Stirring was continued for 2 hr, and then the mixture was poured into 55 ml of 9% aqueous acetic acid. An ether extract of the mixture was washed with aqueous sodium bicarbonate and then with water, dried, and evaporated to give a liquid which rapidly solidified. Crystallization from pentane gave 4.5 g (74%) of prisms: mp 81.5–83.5° (raised to 85–86° on further recrystallization); $\nu_{max}^{CCl_4}$ 820 (aromatic C–H), 3620 and 3650 (OH); pmr spectrum: two singlets, 6 H (δ 0.74, 1.04), *gem*-methyl groups at C-2; doublet (1.20, J = 7 cps) methyl group at C-4, singlet (2.23) methyl group at C-7—which overlap complex absorptions in the region of δ 1.1–3.2; doublet (4.19, J = 8 cps) OH; multiplet, 2 H (6.7–7.2) and broad singlet, 1 H (7.31) aromatic protons.

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.17; H, 9.80.

1,2,4,7-Tetramethylnaphthalene (XXI).—A powdered mixture of 1.7 g of the preceding carbinol and 2 g of freshly fused potassium bisulfate was heated in a distillation apparatus at reduced pressure to give 1.1 g of distillate, bp 122–124°, shown to be a mixture of products (probably tri- and tetramethyldihydronaphthalenes) by means of vpc, infrared, and pmr analyses. A mixture of this distillate, 1.43 g of 2,3-dichloro-5,6-dicyanoquinone (DDQ), and 20 ml of benzene was refluxed for 1 hr, cooled, treated with 20 ml of petroleum ether (bp 30–60°), and filtered to remove the reduced quinone. The filtrate was chromatographed by means of 15 g of Woelm neutral alumina and benzene–petroleum ether (1:1 v/v) as eluent. Vpc analysis of the 610 mg of liquid which remained on evaporation of the effluent showed the presence of 74% of XXI, 11% of mixed trimethylnaphthalenes, and unidentified components therein. Preparative vpc gave XXI as prisms: mp 46–47°; $\nu_{max}^{CS_2}$ 810 s cm^{-1}, 870 s, 881 m, 1015 m, 1035 m, 1172 m, 2930 s, 2950 s, 2980 m, 3020 m; $\nu_{max}^{CHCl_3}$ 1382 s, 1440 s, 1515 s, 1606 s, 1623 s.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.19; H, 8.87.

The picrate formed bright orange needles from absolute ethanol, mp 146–147°.

Anal. Calcd for $C_{20}H_{19}N_3O_7$: C, 58.11; H, 4.63; N, 10.17. Found: C, 57.93; H, 4.76; N, 10.66.

Registry No.—I, 90-15-3; IX, 16020-15-8; X, 16020-16-9; XXI, 16020-17-0; XXI picrate, 16020-18-1; XXVII, 16020-19-2; XXX, 16020-20-5; XXXI, 16020-21-6; methanol, 67-56-1; 1-methoxy-4-methyl-2-naphthaldehyde, 16020-22-7; 1-oxo-2,2-dimethyl-1,2,-3,4-tetrahydronaphthalene, 2,977-45-9.

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