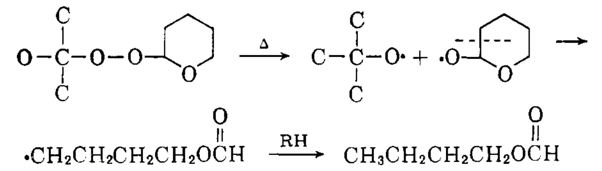
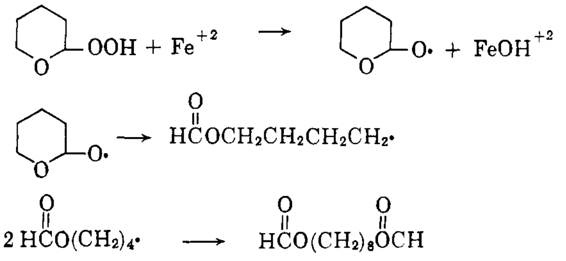
In order to validate further the ester forming steps in the mechanism which require carbon–carbon bond cleavage of a cyclic ether peroxide, the 2-hydroperoxide derivative of 2,5 - dimethyltetrahydrofuran was prepared by autoxidation and decomposed by heating in methyl isobutyl carbinol. The 76% yield of *sec*-butyl acetate supports postulated steps g, h, and i in the reaction sequence.

The methylisobutylcarbinol solvent served as the hydrogen donor to the radicals generated in the decomposition and 0.65 mole of methyl isobutyl ketone per mole of *sec*-butyl acetate formed was actually isolated.

A demonstration that the tetrahydropyran ring can also cleave was shown by the isolation of 39% and 44% yields of *n*-butyl formate when 2-*t*-butylperoxytetrahydropyran was decomposed in methylisobutylcarbinol and di-*n*-butyl ether, respectively. δ-Valerolactone was also produced in *ca.* 15% yield. The extensive ring cleavage observed in the autoxidation of tetrahydropyran is consistent with the same cleavage pattern.



When 2-hydroperoxytetrahydropyran is decomposed by an equivalent amount of ferrous ion in the absence of hydrogen donor—*i.e.*, in aqueous solution, the most important reaction of the intermediate oxy radical is, again, carbon-carbon bond scission with formation of the butyl formate radical. The final product, 1,8-octanediformate has been produced in 50 to 60% yield based on input peroxide. Less important products are *n*-butyl formate and δ-valerolactone[2] in 13 and 3% yields, respectively. This is in distinct contrast with previous descriptions of this system[2] where the major products were reported to be δ-valerolactone and 2-hydroxytetrahydropyran.



Although the actual yields of peroxide are low when 2,5- and 2,6-diols are oxidized, hydroperoxide or hydrogen peroxide is required by the proposed scheme of reaction. Experiments in which hydrogen peroxide replaces oxygen as the oxidizer do, in fact, lead to essentially the same products (Table II). It is further significant that the rate of hydrogen peroxide consumption is greatest in the presence of precisely those glycols, or keto alcohols, where the formation of cyclic hemiketals is most favored (Table I).

Reactions of Methyl-substituted 1,4-Epoxy-1,4-dihydronaphthalenes

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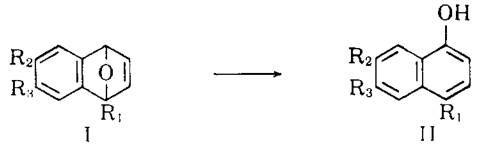
Disruption of the epoxide ring in methyl-substituted 1,4-epoxy-1,4-dihydronaphthalenes by alcohols and a little acid gives alkyl-substituted 1-naphthols when one of the alpha positions contains a hydrogen atom. However, if both the 1- and 4-positions contain methyl groups, the products are substituted 2-naphthols or their derivatives. Furthermore, if the 2- and 3-positions are also occupied by alkyl groups, compounds are formed containing the alkoxymethyl group in the alpha position. Intermolecular condensations also occur under anhydrous conditions.

It has been reported[1] that 1,4-epoxy-1,4-dihydronaphthalene is isomerized nearly quantitatively to 1-naphthol by reaction with methanol containing a little hydrochloric acid. During the course of our work[2] on the synthesis of methyl-substituted anthracenes, a number of methyl-substituted 1,4-epoxy-1,4-dihydronaphthalenes (I) were prepared. The isomerization and other reactions of some of these compounds have now been studied and are reported in this paper.

The first compounds of type I investigated were those in which the 1- and/or 4-positions were occupied by hydrogen. In these cases a little hydrochloric acid in methanol readily caused isomerization to the methyl-substituted 1-naphthols (II) as follows:



I II

Compound no.	R_1	R_2	R_3	Reference
IIa	CH_3	H	H	3
b	H	CH_3	CH_3	4
c	H	CH_3	H	5
d	H	H	CH_3	6

Note: Compounds IIc and d are isomers obtained from the same epoxide.

This method, then, is a fairly convenient one for preparing methyl-substituted 1-naphthols, some of which are otherwise very difficult to prepare.

Naturally the question arose as to what occurs if both the 1- and 4-positions are occupied by methyl or other groups. Such compounds, because of the

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(1) G. Wittig and L. Pohmer, *Ber.*, **89**, 1349 (1956).
(2) E. Wolthuis, *J. Org. Chem.*, **26**, 2215 (1961).
(3) E. Wenkert and T. Stevens, *J. Am. Chem. Soc.*, **78**, 5627 (1956).
(4) E. Coulson, *J. Chem. Soc.*, 1305 (1938).
(5) J. Corran and W. Whalley, *ibid.*, 4719 (1958).
(6) G. DiModica and S. Tira, *Ann. chim.* (Rome), **46**, 838 (1956).

electron-release effect of these groups, should be very susceptible to ring opening, but cannot form 1-naphthols. It was found that these compounds react vigorously with methanol containing a little hydrochloric acid, and that interesting rearrangements take place.

The first such compound to be studied was 1,4-dimethyl-1,4-epoxy-1,4-dihydronaphthalene (III), prepared as reported previously.[2] This compound can be distilled without decomposition at 108–110°/16 mm., a fact not known at the time of the earlier report. In methanol solution, III reacted vigorously with a few drops of concentrated hydrochloric acid, and on cooling, a crystalline product was obtained. Analyses of this product indicate it to be 2-methoxy-1,4-dimethylnaphthalene (IV), identical with that reported,[7] and prepared by methylation of the corresponding naphthol which, in turn, was obtained from desmotroposantonous acid. Further proof of the structure of IV was obtained by its hydrolysis to the known naphthol (V) and the conversion of the latter to 2-acetoxy-1,4-dimethylnaphthalene. Spectral data were found to agree with structure IV.

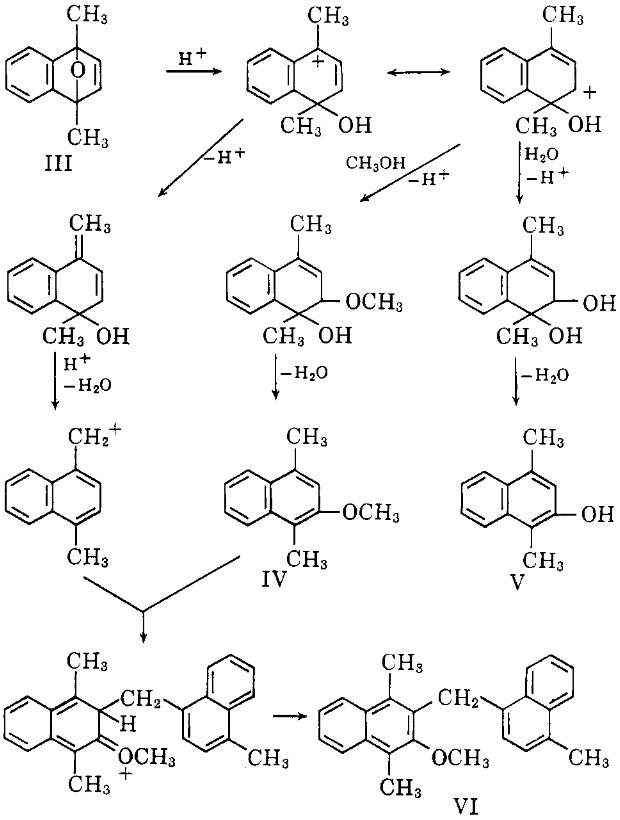
After removal of IV from the reaction mixture, the methanolic liquors contained still other products. One of these, found in small quantity, proved to be the naphthol, V. The other major product, a new compound, was finally assigned the structure VI, which agrees well with all analytical and spectral data, and which was also synthesized by condensing IV with 1-methyl-4-chloromethylnaphthalene.

Having established the fact that reaction of III with methanol and hydrochloric acid gives at least three different products, further studies showed that the relative amounts of these can be varied considerably by altering the reaction conditions. It seemed reasonable that the naphthol, V, should predominate if the reaction were carried out in the presence of more water, and this proved to be correct. With dilute hydrochloric acid alone, III gave up to 69% of V and no IV or VI. The yield of V became progressively lower as the amount of methanol in the reaction mixture was increased, while at the same time the yield of IV increased. High yields of VI were obtained only under anhydrous conditions, such as by reaction in dry methanol with dry hydrogen chloride. In this way III gave about 61% of VI and 26% of IV with only a trace of V.

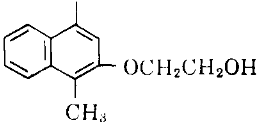
The reactions cited indicate that disruption of the epoxide ring in III results in substitution in the 2-position of the naphthalene ring. The reaction apparently is proton-activated since III is not at all affected by alkalies, and can even be recovered unchanged after boiling with aqueous alkali. It appears likely that the oxygen of the methoxyl or hydroxyl groups is derived from the solvent, but this is still to be determined experimentally.

Although compound VI was at first suspected to be a methyl-substituted dinaphthyl ether, the latter was synthesized by a zinc chloride dehydration of V and found to be other than VI. Spectral and analytical data clearly indicate the structure as shown, apparently the product of a secondary reaction between IV and a carbonium ion intermediate involving the alpha methyl group. On the theory that the intermediate might be 1-methyl-4-chloromethylnaphthalene, attempts were made to isolate this compound from the reaction mixture after a brief reaction of III with dry hydrogen chloride in methanol or hexane. All such attempts failed, but active chlorine was detected by alcoholic silver nitrate after all hydrogen chloride had been removed. That the chloride may be the active intermediate is supported by the facts that (1) it does react with IV to give VI, and (2) the corresponding chloride, X, was isolated when the tetramethyl epoxide (VIII) reacted with dry hydrogen chloride in methanol.

The following mechanism is suggested to account for the formation of IV, V, and VI.



Obviously other alcohols than methanol should also react with III to form comparable 2-alkoxynaphthalenes. Reaction of III with ethylene glycol and a little concentrated hydrochloric acid readily gave the product, VII, in good yield. Although it had been anticipated that both alcoholic functions of ethylene glycol might react to give the dinaphthyl ether of glycol, our experiment produced the mono ether as indicated by the presence of an active hydrogen in the product. Further confirmation of the structure of VII came from analytical and spectral analyses. Its formation can be explained as above for IV.



VII

In view of the products obtained from III, it was interesting to see what would happen if the 2- and 3-positions were blocked to prevent the formation of the 2-naphthol derivatives. Accordingly, 1,2,3,4-tetramethyl-1,4-epoxy-1,4-dihydronaphthalene (VIII)

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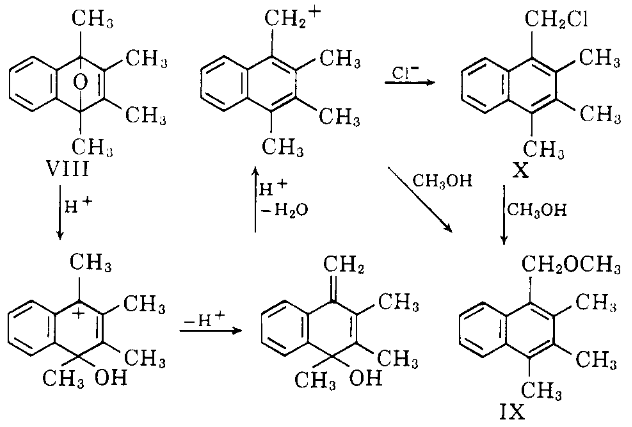
[7] S. Cannizzaro and A. Carnelutti, *Gazz. chim. ital.*, **12**, 407 (1882).

was prepared by a procedure similar to that used to make III. The required 2,3,4,5-tetramethylfuran was prepared by reaction of 3,4-dimethyl-2,5-hexanedione with acetic anhydride.[8] The latter, in turn, was prepared most successfully by reaction of 2-butanone with lead dioxide.[9] Compound VIII reacted readily with methanol and a little concentrated hydrochloric acid to give a 78% yield of 1-methoxymethyl-2,3,4-trimethylnaphthalene (IX). This structure was deduced from elementary analysis, methoxyl determination, and spectral data. The position of the methoxymethyl group was not fixed by these data, but was determined by the fact that compound IX was obtained by reaction of methanol on the previously reported[10] 1-(chloromethyl)-2,3,4-trimethylnaphthalene (X). The latter was obtained in good yield from the epoxide VIII upon reaction with dry hydrogen chloride in methanol, ethanol, or hexane.

It seems likely that IX is formed by the following series of reactions:



The chloride, X, could be isolated only when anhydrous conditions prevailed. It reacted readily with methanol to give IX, and with ethanol to give 1-(ethoxymethyl)-2,3,4-trimethylnaphthalene (XI). All attempts to hydrolyze it to the corresponding alcohol failed, however. Alkaline hydrolysis of X invariably gave a compound to which we have assigned the structure of the ether, bis[2,3,4-trimethylnaphthyl-(1)-methyl] ether (XII). Simply boiling X with water also gave this ether instead of the expected alcohol. Apparently the alcohol, if formed at all, is very easily dehydrated to the ether. Such behavior also has been reported[11] for a similar compound, namely, 1-(chloromethyl)-4-methylnaphthalene.

Attempts to make the alcohol from X by indirect methods also failed. For example, X reacted with lead or silver acetate to form the acetate, which was then hydrolyzed with alkali, but the product again was the ether, XII.

One other epoxide was made for study of its reactions, 1,4-dimethyl-2,3-diethyl-1,4-epoxy-1,4-dihydronaphthalene (XV). It was made by condensation of benzyne with 2,5-dimethyl-3,4-diethylfuran (XIV), which was prepared from 3,4-diethyl-2,5-hexanedione (XIII). The latter was derived from 2-pentanone by oxidation with lead dioxide. The behavior of the epoxide (XV) was not studied extensively, but we report in the Experimental what has been done with it.

Experimental[12]

4-Methyl-1-naphthol (**IIa**).—1-Methyl-1,4-epoxy-1,4-dihydronaphthalene[2] 0.791 g. (5 mmoles) was dissolved in a warm mixture of 5 ml. methanol and 1 ml. of water, 3 ml. of concentrated hydrochloric acid was added, and the mixture was boiled under reflux 15 min. After removal of the methanol, the residue was dissolved in 20 ml. of water and 0.3 g. of sodium hydroxide. The warm solution was filtered with carbon and the filtrate acidified to precipitate the product. Filtration, washing, and drying gave 0.700 g. (88%) of IIa, m.p. 78–80°. Recrystallization from ligroin gave 0.620 g., m.p. 82–83° (lit.,[3] 83–84°).

6,7-Dimethyl-1-naphthol (**IIb**).—6,7-Dimethyl-1,4-epoxy-1,4-dihydronaphthalene,[2] 1.722 g. (10 mmoles), was dissolved in 20 ml. of warm methanol, 2 drops of concentrated hydrochloric acid was added, and the mixture refluxed 10 min. After removal of the methanol, the residue was extracted with hot, dilute sodium hydroxide solution, clarified with carbon, and filtered. The filtrate was acidified, cooled, and filtered, and the residue dried to give 1.22 g. (71%), m.p. 138.5–139.5°. Recrystallization of a part of it from benzene-petroleum ether gave m.p. 139–139.5° (lit.,[4] 140°).

6(**and** 7)-**Methyl-1-naphthol** (**IIc and d**).—6-Methyl-1,4-epoxy-1,4-dihydronaphthalene,[2] 0.700 g. (4.4 mmoles), in 10 ml. of warm methanol was treated with 2 drops of concentrated hydrochloric acid and refluxed for 10 min. The solvent was removed and the residue was dissolved in warm hexane, decolorized with carbon, filtered, and cooled thoroughly. Filtration and washing of the crystals gave 0.340 g. (49%) of IIc, m.p. 102–105°. One recrystallization from hexane gave m.p. 105–107° (lit.,[5] 111°), but it was not further purified. The liquors from the first crop of crystals were evaporated to dryness, the residue was extracted with hot, dilute sodium hydroxide solution, clarified with carbon, and the clear filtrate acidified to give 0.100 g. (14%) of IId, m.p. 80–83°, not further purified (lit.,[6] m.p. 83°).

1,4-Dimethyl-2-methoxynaphthalene (**IV**).—1,4-Dimethyl-1,4-epoxy-1,4-dihydronaphthalene (III),[2] 1.502 g. (8.73 mmoles), was dissolved in 15 ml. of methanol, heated to boiling, and 10 drops of concentrated hydrochloric acid were added. A vigorous reaction ensued, after which the mixture was held at reflux for 0.5 hr. and then cooled overnight in a refrigerator. Filtration and washing with cold methanol gave 0.422 g. (26%) of crystals, m.p. 66–67.5°. The filtrate was evaporated to dryness, the residue taken up in hexane and put through a column of alumina. The first fractions through the column contained another 0.487 g. (30%) of IV, m.p. 66.5–66.8°. Recrystallization from methanol gave m.p. 68.4–68.8° (lit.,[7] 68°). Further elution with hexane containing 5% methanol gave 0.267 g. of a semisolid fraction which was recrystallized twice from methanol to give 0.125 g. of VI, m.p. 152–153°. The alumina retained a fraction, fluorescing strongly in the ultraviolet, which was extracted with boiling methanol to give a very small amount of the naphthol, V, m.p. 132–133°.

Anal. of IV. Calcd. for $C_{13}H_{14}O$(186.2): C, 83.83; H, 7.58; OMe, 16.63; mol. wt., 186. Found: C, 83.92; H, 7.51; OMe, 16.58; mol. wt. (Rast), 180.

Ultraviolet spectrum in C_6H_{12}: λ_{max} mμ (log ϵ): 235.5 (4.96), 288 (3.84), 300 (3.81), 327 (3.53), 337 (3.50), 342 (3.55). Infrared spectrum showed a broad absorption at 1200–1300 cm.$^{-1}$ indicative of an ether.

1,4-Dimethyl-2-naphthol (**V**).—A 0.294-g. sample (1.71 mmoles) of III was heated for 5 min. at 90–100° with 10 ml. of water and 2 drops of concentrated hydrochloric acid. The mixture became cloudy at once and an oil separated which solidified on cooling. Extraction of the solid with warm, dilute sodium hydroxide solution, clarification with carbon, and acidification of the clear filtrate gave 0.202 g. (69%) of V, m.p. 130–132°. Recrystallization from ligroin gave m.p. 133–133.5° (lit.,[7] 135–136°). Upon

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(8) R. Gaertner and R. Tonkyn, *J. Am. Chem. Soc.*, **73**, 58 (1951).

(9) A. Wolf, German Patent 876237 (1953).

(10) C. L. Hewett, *J. Chem. Soc.*, 293 (1940).

(11) G. Lock and R. Schneider, *Ber.*, **91**, 1770 (1958).

(12) The authors are grateful to Dr. J. L. Johnson and his staff at the Upjohn Co., Kalamazoo, Mich., for determining all spectra reported herewith, and especially to Dr. G. Slomp for assistance in interpreting the n.m.r. spectra. All melting and boiling points are uncorrected. N.m.r. spectra were observed on Varian A-60 and DP-60 spectrometers operating at 60 Mc. on solutions of the samples in chloroform. The spectra were calibrated in c.p.s. downfield from internal tetramethylsilane.

acetylation there was obtained 2-acetoxy-1,4-dimethylnaphthalene, m.p. 76–77°, from methanol (lit.,[7] 77–78°).

1-(4-Methylnaphthyl)-2-(3-methoxy-1,4-dimethyl)naphthylmethane (VI). Method A.—Dry hydrogen chloride was passed into a boiling solution of 1.056 g. (6.1 mmoles) of III in 15 ml. of dry methanol for 1.5 hr. The solution turned brown and a precipitate formed. After refrigeration overnight, the precipitate was filtered off, washed with cold methanol, and dried to give 0.552 g. (53%) of VI, m.p. 144–148°. Recrystallization from hexane gave colorless needles, m.p. 152.5–153°. The liquors were evaporated to dryness below 100° and the residue extracted with hexane to give another 0.100 g. (10%), m.p. 145–148°.

Anal. of pure product. Calcd. for $C_{25}H_{24}O$ (340.4): C, 88.20; H, 7.11; OMe, 9.1. Found: C, 88.17; H, 7.19; OMe, 9.0.

Ultraviolet spectrum in ethanol; $\lambda_{\max}$ mμ (log ε): 226.5 (4.90), 239 (4.89), 279 sh (4.11), 289 (4.20), 299 sh (4.08), 314 sh (3.40), 331 (3.41), 344 (3.38). Infrared spectrum showed bands due to aromatic ether at 1000–1050 and 1200–1300 cm.$^{-1}$. N.m.r. spectrum indicated 4 kinds of H: 3 singlets at 149, 155, and 159 c.p.s. due to 3 similar aromatic Me groups, a singlet at 231 c.p.s. (arom. OMe), a singlet at 273 c.p.s. (CH_2) and 5 kinds of absorptions at 422–490 c.p.s. (10 aromatic H atoms).

Method B.—A 0.30-g. sample (1.63 mmoles) of IV, 0.32 g. of 1-chloromethyl-4-methylnaphthalene, and 2.2 g. of anhydrous zinc chloride were heated for 4 hr. at reflux temperature in 25 ml. of dry toluene. After excess zinc chloride had been removed by filtration, the filtrate was evaporated to dryness, the residue taken up in hexane, the solution clarified with carbon and evaporated to give 0.27 g. (48%) of VI, m.p. 146–148°; after recrystallization from hexane, m.p. 151.2–152.2°. A mixed melting point with VI obtained by method A showed no depression, and the spectra were identical in every detail.

2-(1,4-Dimethyl-2-naphthoxy)ethanol (VII).—A 1.047-g. sample (6.1 mmoles) of III was dissolved in 25 ml. of ethylene glycol. Two drops of concentrated hydrochloric acid were added, whereupon the temperature rose 5°. The mixture was refluxed 15 min., cooled, and 25 ml. of 1% aqueous sodium hydroxide was added. Upon cooling, the product separated, was filtered off, washed twice with water, and then dried to give 1.05 g. (80%) of VII, m.p. 98–99.5°. Recrystallization from benzene gave 0.92 g., m.p. 102.8–103.0°. The alkaline filtrate (above) had a blue-green fluorescence, but on acidification gave only a trace of the naphthol, V.

Anal. Calcd. for $C_{14}H_{16}O_2$ (216.3): C, 77.75; H, 7.46. Found: C, 78.03; H, 7.37.

Ultraviolet spectrum in ethanol, $\lambda_{\max}$ mμ (log ε): 214 sh (4.32), 234 (4.81), 265 sh (3.41), 277.5 sh (3.65), 286.5 (3.76), 297 (3.69), 326 (3.34), 338 sh (3.30). Infrared spectrum showed strong bands at 1200–1300 (aryl C—O) and 3200 cm.$^{-1}$ (OH). N.m.r. spectrum: 149 and 154 c.p.s. due to two aromatic Me groups, a singlet shifting to 166 c.p.s. on dilution (OH hydrogen), 240 c.p.s. (two CH_2 groups), 421 c.p.s. (one aromatic H), 444 and 473 c.p.s. (four adjacent aromatic H).

3,4-Dimethyl-2,5-hexanedione.—Butanone, 300 g., and lead dioxide, 100 g., were heated for 23 hr. at 78° under reflux. The mixture was filtered and the filtrate dried over calcium chloride and fractionated. After unchanged butanone had been distilled the product, 23.3 g. (39%), distilled at 101–107°/34 mm. (lit.,[9] 90–105°/18 mm.), n^{20}_{D} 1.430.

2,3,4,5-Tetramethylfuran.—3,4-Dimethyl-2,5-hexanedione, 71 g., acetic anhydride, 59 g., and anhydrous zinc chloride 6 g., were heated slowly to reflux temperature and then held there for 3 hr. After addition of 200 ml. of 6 *N* aqueous sodium hydroxide, the product was removed by steam distillation and extracted from the distillate with ether. The extract was dried over calcium chloride, the ether removed, and the product distilled to give 30 g. (49%) at 65–70°/42 mm. (lit.,[8] 92.5–94°).

1,2,3,4-Tetramethyl-1,4-epoxy-1,4-dihydronaphthalene (VIII). Method A.—*n*-Butyllithium in ether, 120 ml. of 0.95 *N*, was added to a flask previously evacuated and filled with pure nitrogen, and cooled to −65°. There was added 35.6 g. of 2,3,4,5-tetramethylfuran, and then 23.6 g. (0.1 mole) of *o*-dibromobenzene during 40 min. at −65 to −60°. The mixture was allowed to warm to 0°, and 200 ml. of water was added. The layers were separated, the aqueous layer was washed twice with ether, the washes were added to the ether layer which was then washed twice with water and dried over potassium carbonate. The ether and unchanged tetramethylfuran (24.6 g.) were removed by distillation, and the oily residue was taken up in hexane and cooled to give 10.0 g. (50%) of VIII, m.p. 41–46°. Recrystallization from hexane gave m.p. 45.6–46°.

Method B.—Magnesium turnings, 5.4 g. (0.22 g.-atom), and 20 ml. of dry tetrahydrofuran were added to a flask, previously evacuated and filled with dry nitrogen. 1-Fluoro-2-bromobenzene, 35.0 g. (0.20 mole), was dissolved in 50 ml. of tetrahydrofuran, and 3–5 ml. of this solution was added to the flask to start the reaction, keeping the temperature below 40°. 2,3,4,5-Tetramethylfuran, 33.7 g. (0.272 mole), in 20 ml. of tetrahydrofuran was then added, after which the remainder of the fluorobromobenzene solution was added during about 0.5 hr. at 35–40°. After reaction had ceased, the mixture was stirred 2–3 hr. more and allowed to stand 5–6 hr. There was added a solution of ammonium chloride, 100 g. in 350 ml. water, made alkaline with ammonium hydroxide, the layers were separated, the aqueous layer was washed with ether and the washes were added to the tetrahydrofuran layer. The entire extract was then washed with 0.1 *N* ammonium hydroxide, 400 ml., separated, and dried over potassium carbonate. The ether and tetrahydrofuran were removed by distillation, and further vacuum distillation gave 5.1 g. of tetramethylfuran and then 29.5 g. (74%) of VIII distilling at 130–132.5°/16 mm. Recrystallization from hexane gave 24.8 g. (62%), m.p. 44–46°.

Anal. of pure compd. Calcd. for $C_{14}H_{16}O$ (200.3): C, 83.96; H, 8.05. Found: C, 84.06; H, 8.09.

Ultraviolet spectrum in ethanol: $\lambda_{\max}$ mμ (log ε): 247.5 (283), 258.5 (2.84), 265 (2.90), 272.5 (2.99), 279 (2.93). Infrared bands were prominent at 1250–1300 (—C—O—C—) and 680–880 cm.$^{-1}$ (Ar C—H deformation).

1-(Methoxymethyl)-2,3,4-trimethylnaphthalene (IX). Method A.—A 0.50-g. sample (2.5 mmoles) of VIII was dissolved in 10 ml. of warm methanol, and 3 drops of concentrated hydrochloric acid was added. The solution turned light red in color, was refluxed 20 min. and then cooled at 0° several hours. The crystals were filtered off and washed with cold methanol. Additional product was obtained from the liquors by evaporation and cooling; total yield: 0.42 g. (78%), m.p. 75.5–76.2°, not increased on recrystallization.

Method B.—A 0.20-g. sample of X was dissolved in 3 ml. of boiling methanol. Upon cooling thoroughly, there was obtained a quantitative yield of IX, m.p. 72–75.5°. Recrystallization from methanol gave m.p. 75.5–76.2°.

Anal. Calcd. for $C_{15}H_{18}O$ (214.3): C, 84.06; H, 8.47; OMe, 14.48. Found: C, 84.30; H, 8.44; OMe, 14.42.

Ultraviolet spectrum in ethanol: $\lambda_{\max}$ mμ (log ε): 228 sh (4.82), 233 (4.95), 280 (3.77), 290 (3.83), 300 sh (3.69), 320 sh (2.70), 324 (2.67). A strong infrared absorption at 1050–1100 cm.$^{-1}$ indicated the —C—O—Me group. N.m.r.: 144, 149, and 157 c.p.s. due to 3 similar aromatic Me groups, 208 c.p.s. (aliphatic OMe), 295 (CH_2), 443 and 483 c.p.s. (four adjacent aromatic hydrogens).

1-(Chloromethyl)-2,3,4-trimethylnaphthalene (X).—Dry hydrogen chloride was passed through a solution of 3.0 g. (1.495 mmoles) of VIII in 30 ml. of dry methanol for 20 min. The solution turned very dark. After cooling thoroughly, the product was filtered off and washed with cold methanol; yield: 2.6 g. (79%). Recrystallization from hexane gave 2.1 g. (64%), m.p. 94.5–95.5° (lit.,[10] 94–95°).

This reaction was also run in other solvents with the yields: hexane, 65.4%; ethanol, 59.4%.

Anal. Calcd. for $C_{14}H_{15}Cl$ (218.73): Cl, 16.21. Found: Cl, 16.03.

Ultraviolet spectrum in ethanol: $\lambda_{\max}$ mμ (log ε): 229 sh (4.83), 233 (4.93), 291 (3.85), 326 sh (2.81).

1-(Ethoxymethyl)-2,3,4-trimethylnaphthalene (XI). Method A.—Using the procedure of method A for IX except substituting ethanol for methanol, 0.50 g. of VIII gave 0.45 g. (79%), m.p. 52–55°. Recrystallization from ethanol gave 0.27 g. (47%), m.p. 58.2–58.8°.

Method B.—Substituting ethanol for methanol in method B for IX, 0.65 g. of X gave 0.55 g. (81%), m.p. 55–56.5°, not further purified.

Anal. of pure XI: Calcd. for $C_{16}H_{20}O$ (228.34): C, 84.16; H, 8.83. Found: C, 84.10; H, 8.76.

Ultraviolet spectrum in ethanol: $\lambda_{\max}$ mμ (log ε): 228 sh (4.83), 233 (4.96), 282 sh (3.79), 290 (3.84), 300 sh (3.70). Infrared absorptions at 1065 (CH_2O) and 1100 (—C—O—C—) cm.$^{-1}$.

Bis[2,3,4-trimethylnaphthyl-(1)-methyl] Ether (XII).—A solution of 1.8 g. (8.23 mmoles) of X in 30 ml. of 30% potassium hydroxide was refluxed for 2 hr. After dilution and cooling, the solid product was filtered off and washed free of alkali; yield: 1.4 g. crude. Two recrystallizations from ethanol gave 0.75 g., m.p. 190–190.5°. The liquors were evaporated to dryness, the residue was dissolved in hexane and run through a column of alumina to give, first, 0.11 g. of a compound not yet identified, m.p. 57–58°, and then 0.32 g., m.p. 189–90°. The total yield of XII was 1.07 g. (68%); mol. wt. (Rast), 396 (calcd. 382).

Anal. Calcd. for $C_{28}H_{30}O$ (382.52): C, 87.91; H, 7.91. Found: C, 86.72; H, 7.89.

Ultraviolet spectrum in ethanol: λ_{max} mμ (log ϵ): 228 (5.11), 233 (5.13), 283 sh (4.08), 292 (4.16), 301 sh (4.06). Infrared absorption shows a broad band at 1000–1100 cm.$^{-1}$ indicating the —C—O—C— group. N.m.r.: 143, 148, and 157 c.p.s. due to six methyl groups; 307 c.p.s. (two CH_2 groups); 436–490 c.p.s. (eight aromatic hydrogen atoms).

3,4-Diethyl-2,5-hexanedione (XIII).—A 400-g. sample (4.64 moles) of 2-pentanone and lead dioxide, 530 g. (2.22 moles), were heated together at reflux temperature for 27 hr. The lead oxide was removed by filtration and washed with ether. The filtrate and washings were dried over calcium chloride and distilled to give 10 g. of recovered pentanone and then 50.7 g. (13.4%) of XIII, b.p. 112–115°/20 mm., n^{20}_D 1.446.

Anal. Calcd. for $C_{10}H_{18}O_2$ (170.24): C, 70.57; H, 10.55. Found: C, 72.18; H, 10.81.

2,5-Dimethyl-3,4-diethylfuran (XIV).—A 93.0-g. sample (0.546 mole) of XIII, 70 g. (0.69 mole) of acetic anhydride, and 7.0 g. of anhydrous zinc chloride were warmed together slowly until an exothermic reaction began. The reaction was moderated by cooling with water, and finally the mixture was heated at reflux temperature for 3 hr. (A shorter time may be desirable, since charring seemed to increase with time.) After making alkaline by addition of 50 ml. of 40% sodium hydroxide, the furan was distilled with steam. The layers in the distillate were separated, the aqueous layer was extracted with ether and the extract added to the crude furan layer. After drying over calcium chloride, vacuum distillation gave 40.2 g. (48.5%) of XIV, b.p. 67–69°/17 mm., n^{20}_D 1.458.

Anal. Calcd. for $C_{10}H_{16}O$ (152.23): C, 78.89; H, 10.60. Found: C, 77.93; H, 10.48.

1,4-Dimethyl-2,3-diethyl-1,4-epoxy-1,4-dihydronaphthalene (XV).—Using method B described above for the preparation of VIII, 36.4 g. of XIV gave 26.2 g. (57.5%) of XV, b.p. 152–154°/18 mm. Recrystallization from hexane gave 22.5 g. (49.4%) of XV, m.p. 50–52°. Another recrystallization gave m.p. 51.6–52.3°.

Anal. Calcd. for $C_{16}H_{20}O$ (228.32): C, 84.20; H, 8.76. Found: C, 84.16; H, 8.76.

Ultraviolet spectrum in ethanol: λ_{max} mμ (log ϵ): 250 (2.89), 265 (2.92), 272.5 (3.00), 280 (2.92). Infrared absorptions at 1250–1300 (—C—O—C—) and 680–880 cm.$^{-1}$ (Ar C—H deformation).

1-Chloromethyl)-4-methyl-2,3-diethylnaphthalene (XVI).—Dry hydrogen chloride was passed into a solution of 2.08 g. (8.76 mmoles) of XV in 30 ml. dry methanol. After 20 min. the solution, now dark in color, was refrigerated, the crystals were filtered off and washed with cold methanol; yield: 1.8 g. (84.5%). Recrystallization from hexane gave 1.2 g. (56.4%) of pure XVI, m.p. 72.5–73°.

Anal. Calcd. for $C_{16}H_{19}Cl$: Cl, 14.32. Found: Cl, 13.85.

Ultraviolet spectrum in ethanol: λ_{max} mμ (log ϵ): 230 sh (4.80), 235.5 (4.98), 293 (3.86), 329 sh (2.87).

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Catalytic Hydrogenation of α,β-Unsaturated Ketones. III. The Effect of Quantity and Type of Catalysts[1,2]

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The relative amounts of *cis*- and *trans*-β-decalone obtained on hydrogenation of $\Delta^{1,9}$-octalone-2 using varying amounts of 10% palladium–charcoal catalyst has been determined in acidic, basic, and neutral media. In all cases, a sharp change in the per cent of *cis* isomer formed was observed at a palladium–substrate ratio of 1:100. This corresponded to the point of inflection of the rate *vs.* quantity of catalyst curve. The effect of platinum and rhodium as catalysts was also determined.

In line with other work on the hydrogenation of α,β-unsaturated ketones,[1] it was considered important to study the effect of the quantity of catalyst on the stereospecificity of the reaction. To do this a series of hydrogenations of $\Delta^{1,9}$-octalone-2 (I) using a wide variety of catalyst–substrate ratios were run. The amounts of *cis*-β-decalone (II) obtained in acidic, basic and neutral medium hydrogenations using different weights of 10% palladium on charcoal to hydrogenate 250 milligrams of I are shown in Fig. 1. It is of interest to note that the stereospecificity in acid medium shows a maximum at a palladium–octalone ratio of 1:100 while in neutral and basic media a minimum in the percent of II obtained occurs at the same point.

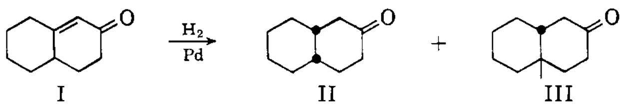
I II III

Fig. 2 shows the per cent of II obtained using fifty milligrams each of different percentages of palladium on charcoal in the hydrogenation of I. The results shown here are not so clear as those in Fig. 1. Young and Hartung have stated that varying the metal to carrier ratio of palladium-on-charcoal catalysts can also vary the number of palladium atoms in a given cluster, the spacing between these clusters and, possibly, even the crystalline lattice structure of the metal as well.[3] It is possible, then, that the activity of the catalyst as well as its stereospecificity could be effected by changing any of these variables. In the case where the weight of catalyst was varied the metal to carrier ratio remained constant and the above mentioned variables were eliminated. The following discussion will concern itself only with this latter type of system.

The rates of the various reactions are shown in Fig. 3. These rates represent the volume of hydrogen taken up in the time between five and fifteen minutes after the initiation of the reaction keeping the hydrogen pressure and the stirring rate constant. The re-

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(1) Part II in this series; R. L. Augustine and A. D. Broom, *J. Org. Chem.*, **25**, 802 (1960).

(2) Support for this work by the National Institutes of Health through Research Grant RG9696 from the Division of General Medical Sciences, U. S. Public Health Service, is gratefully acknowledged.

(3) J. G. Young and W. H. Hartung, *J. Org. Chem.*, **18**, 1659 (1953).