[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

THE REACTION OF SOME OLEFIN OXIDES WITH THE NAPHTHOLS

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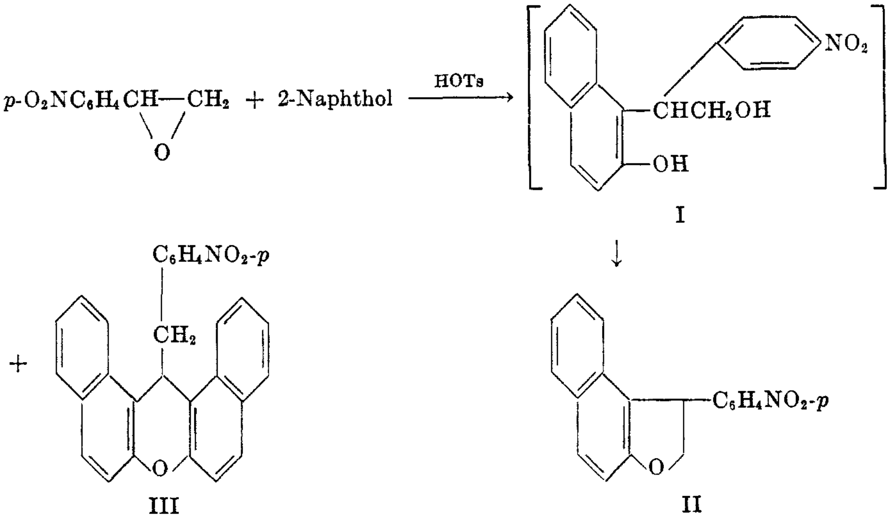
In order to add to the existing knowledge of the chemistry of olefin oxides, particularly the factors that govern the direction of ring opening in unsymmetrical oxides, the reactions of several styrene oxides with various phenols have been studied and reported (1–8). The present report describes the reactions of some of these styrene oxides and of cyclohexene oxide with the naphthols, principally with 2-naphthol. The reactions of these styrene oxides with 2-naphthol were found to deviate somewhat from those reported with phenol in that more nuclear attack was observed, probably a result of the greater nucleophilic character of the naphthol nucleus. Cyclohexene oxide was included in this study to ascertain whether it would be similar in behavior to propylene oxide, as might be expected, in contrast to styrene oxide. The postulated importance (1, 3, 4, 6) of a resonance-stabilized intermediate in the reactions of the styrene oxides to form primary alcohols is again further supported by these experimental results.

The reaction of *p*-nitrostyrene oxide with 2-naphthol was carried out at 100° with excess 2-naphthol and acid catalysis. From the reaction mixture only a dihydrofuran (II)(38.1%) and a xanthene (III)(5.4%) could be isolated.



The dihydrofuran was presumed to result from nuclear attack to form a phenolalcohol (I), as shown, followed by cyclization, whereas the xanthene probably was formed by way of an initial isomerization of the oxide to *p*-nitro-

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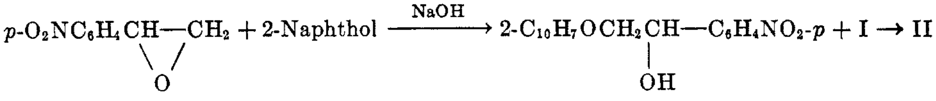
[2] This paper is based on a portion of the Ph.D. dissertation (1951) of Rudolph Rosenthal.

phenylacetaldehyde. This aldehyde then condensed with 2-naphthol to form the xanthene. Phenylacetaldehyde and 2-naphthol, as an analogous example, are known to undergo an acid-catalyzed reaction to give a xanthene (9). The structures of II and III were proved by reduction and deamination to known compounds.

With aqueous sodium 2-naphthoxide and excess 2-naphthol the reaction of *p*-nitrostyrene oxide produced a mixture from which the ether-alcohol (IV) (20.3%) was isolated as an alkali-insoluble component. Again, the structure of IV was proved by reduction and deamination. An alkali-soluble product was also indicated, so this fraction was subjected to the conditions conducive to the acid-catalyzed cyclization of I. In this manner a 21.4% yield of II was obtained. The corresponding reaction of this oxide with sodium phenoxide has been shown (4)



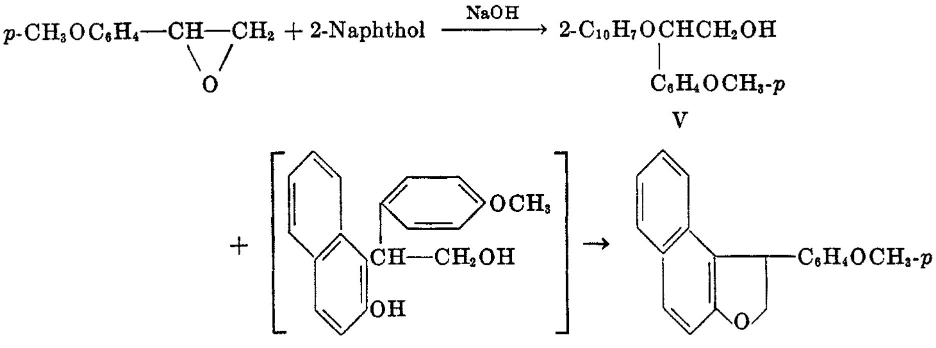
$$p\text{-}O_2NC_6H_4CH\underset{\diagdown O \diagup}{—}CH_2 + \text{2-Naphthol} \xrightarrow{\text{NaOH}} \text{2-}C_{10}H_7OCH_2\underset{\substack{| \\ OH}}{CH}—C_6H_4NO_2\text{-}p + \text{I} \rightarrow \text{II}$$

IV

to give an excellent yield of a mixture of the etheralcohols, but nothing analogous to I then was detected nor could have been present in more than a very small amount (4).

p-Methoxystyrene oxide, in the acid-catalyzed reaction with 2-naphthol, gave alkali-insoluble products from which a small amount (11.9%) of a compound presumed to be 14-*p*-methoxybenzyl-14*H*-dibenzo[*a*, *j*]xanthene, comparable to III, was isolated.

The reaction of *p*-methoxystyrene oxide with aqueous sodium 2-naphthoxide and excess 2-naphthol produced a mixture from which the ether-alcohol (V) (30.7%) was readily isolated. When the alkali-soluble fraction of the reaction mixture was refluxed in benzene with *p*-toluenesulfonic acid to cyclize any of the phenolalcohol (VI) present, the dihydrofuran (VII)(39.4%) resulted. These structures were proved by alternative methods of synthesis. The combined yields obtained here with 2-naphthol were considerably higher than from the oxide-phenol reaction (6); the incidence of nuclear attack was also greater with 2-naphthol.

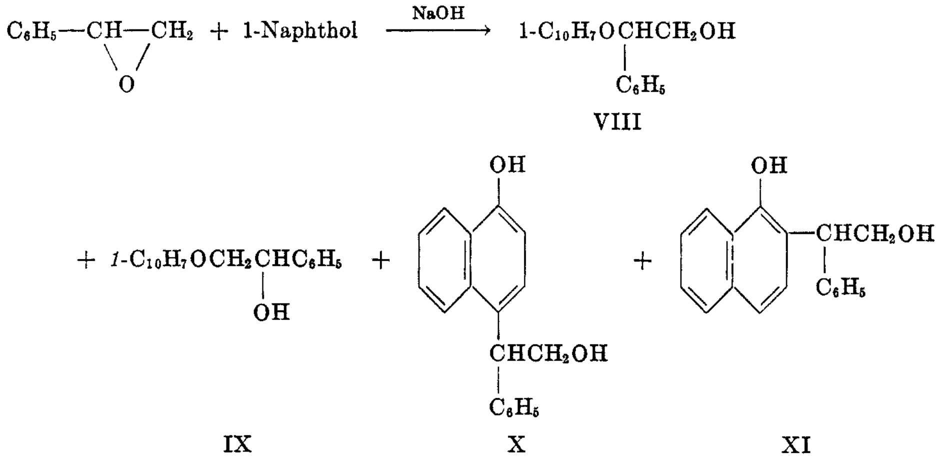


V

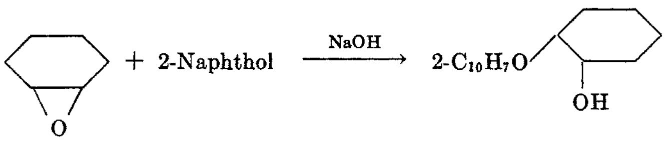
VI

VII

In an earlier study (2) of the reaction of styrene oxide with aqueous sodium 2-naphthoxide, the predominant product was the phenol-primary alcohol resulting from nuclear attack; a lesser amount of the ether-primary alcohol was also found. In our present work, the reaction of styrene oxide with aqueous sodium 1-naphthoxide and excess 1-naphthol led to at least four different products (VIII, IX, X, and XI). The mixture of alkali-insoluble products (VIII and IX) was obtained in a crude yield of 30.3% with the primary alcohol (VIII) predominating. Separation of these alcohols was accomplished by selective esterification with phthalic anhydride. The alkali-soluble components (X and XI) were separated by cyclizing XI to the corresponding dihydrofuran (28.5%), thus enabling X to be isolated in 9.1% yield. The structures of all of the isolated products were proved by synthesis by other methods.

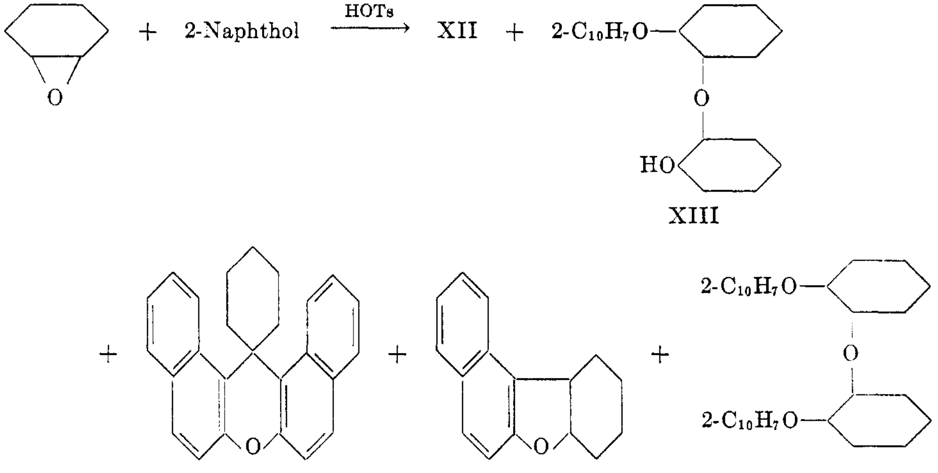


The reaction of cyclohexene oxide with aqueous sodium 2-naphthoxide afforded one product, the ether-alcohol (XII) in 86.8% yield. The structure of XII was assumed on the basis of the method of formation, the carbon and hydrogen analyses, and the formation of a *p*-nitrobenzoate. The purity of the recovered 2-naphthol from the alkali-soluble portion of the reaction mixture indicated that nuclear attack to form a phenolalcohol was completely absent. All of the styrene oxides, on the other hand, have given phenolalcohols in their reactions with the naphthols.



XII

In contrast, the acid-catalyzed reaction of cyclohexene oxide with 2-naphthol was relatively complicated in that several secondary reactions appeared to occur. Five products were isolated in a combined yield of 38.7%. The etheralcohol (XII) was isolated in 21.5% yield, mainly by fractional recrystallization. The remaining compounds were adsorbed on an alumina column and were fractionally eluted with various solvents. In this way the dietheralcohol (XIII) was obtained in a 8.2% yield, the xanthene (XIV) in 3.7% yield, the furan (XV) in 3.1% yield, and the triether (XVI) in 2.2% yield.



XIII

XIV XV XVI

The structures assigned (XIII–XVI) followed from seemingly rational deductions, the chemical behavior, carbon and hydrogen analyses, molecular weight determinations, and certain conversions that could be effected. For example, the xanthene (XIV) was also formed, it was found, in the reaction of the ether-alcohol (XII) with 2-naphthol in the presence of *p*-toluenesulfonic acid. The product shown as XIII resulted when the ether-alcohol (XII) was treated with excess cyclohexene oxide under the conditions of the original reaction. Although the triether (XVI), if the assigned structure is correct, might conceivably have been formed from two molecules of XII or from XIII and 2-naphthol, attempts to prepare XVI by either method were unsuccessful. The case for the furan structure (XV) was based on analyses and the lack of any evidence for unsaturation with bromine in carbon tetrachloride. Assuming that the assigned structure is correct, this compound could have been formed by nuclear attack by the oxide, followed by cyclization of the resulting phenolalcohol, or by the cyclization of XII. In any event, our presumed furan (XV), m.p. 56–57.5°, did not agree in melting point with the same compound reported by Niederl, Niederl, and Charney (10), m.p. 66–68°, as one of two probable products from the reaction of cyclohexanone with 2-naphthol. Of course, the structure XV may exist in stereoisomeric forms, so a discrepancy need not necessarily be present.

EXPERIMENTAL[3]

p-Nitrostyrene oxide and 2-naphthol, acid-catalyzed. In a 100-ml., three-necked flask fitted with a stirrer and condenser was placed 2-naphthol (10.4 g., 0.072 mole) which then

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[3] All temperature measurements are uncorrected. Microanalyses are by the Elek Micro Analytical Laboratories and by Mr. Joseph Pirie of this Department.

was heated in an oil-bath to 140°. The bath was cooled to 120° and *p*-toluenesulfonic acid (0.1 g.) was added. *p*-Nitrostyrene oxide (4) (4.0 g., 0.024 mole) was added with stirring, and the bath was immediately cooled to 100°. After 20 minutes at this temperature the red, one-phase mixture was taken up in benzene (200 ml.), extracted with 4% sodium hydroxide (200 ml.), washed with water, and the benzene was removed to obtain a brown oil (6.3 g.). This oil was redissolved in benzene and passed through an alumina column. Removal of the solvent left a residue (4.0 g.) which, if it did not solidify, was warmed with absolute ethanol to induce crystallization. The product then was heated with 80% ethanol (100 ml.), filtered while hot, the filtrate was saved, and the insoluble residue was recrystallized from glacial acetic acid. Thus there was obtained 0.54 g. (5.4%), needles, m.p. 187–189°. The analytical sample melted at 189.5–190°. This material was shown to be *14-p-nitrobenzyl-14H-dibenzo-[a,j]xanthene* (III).

Anal. Calc'd for $C_{28}H_{19}NO_3$: C, 80.56; H, 4.59; N, 3.36.
Found: C, 80.73; H, 4.79; N, 3.52.

Proof of structure was accomplished by reduction of the nitro group to the amine with Raney nickel in absolute alcohol (4). This amine then was deaminated by the procedure of Kornblum and Iffland (11) with hypophosphorous acid and sodium nitrite to give 14-benzyl-14*H*-dibenzo[*a,j*]xanthene (53.8%), m.p. 177–178° (9) alone or when mixed with an authentic sample.

The 80%-ethanol filtrate, mentioned in the foregoing, was extracted with benzene, the benzene layer was washed with water and the benzene was removed. The residual oil was recrystallized from absolute ethanol to give 2.67 g. (38.1%), m.p. 123–126°, of *1-p-nitrophenyl-1,2-dihydronaphtho[2,1-b]furan* (II) as shown by reduction and deamination, as before, to a known compound, 1-phenyl-1,2-dihydronaphtho[2,1-*b*]furan, m.p. 95–96° alone or when mixed with an authentic sample (12). The analytical sample melted at 126–127°.

Anal. Calc'd for $C_{18}H_{13}NO_3$: C, 74.21; H, 4.50; N, 4.81.
Found: C, 74.11; H, 4.66; N, 4.96.

In the structure proof of this furan the intermediate obtained by reduction of the nitro group, *1-p-aminophenyl-1,2-dihydronaphtho[2,1-b]furan*, was isolated by evaporation of the ethanol used as a solvent in the reduction. This amine was recrystallized from ethanol, white needles, m.p. 135–136°, turning pink on contact with air.

Anal. Calc'd for $C_{18}H_{15}NO$: N, 5.36. Found: N, 5.21.

All attempts to isolate other products from this oxide-2-naphthol reaction failed.

p-Nitrostyrene oxide and sodium 2-naphthoxide. In the same apparatus used in the foregoing was placed 2-naphthol (5.2 g., 0.036 mole) and sodium hydroxide (0.5 g., 0.012 mole) in water (10 ml.). To this stirred mixture, at 85°, was added *p*-nitrostyrene oxide (2.0 g. 0.012 mole). The red solution was held at 85° for 20 minutes (a longer time, up to two hours, gave the same results), then taken up in benzene (200 ml.) and extracted with 4% sodium hydroxide (200 ml.), the alkaline extract being reserved. The benzene solution was washed with water and the benzene removed to obtain a light tan oil (2.8 g.). This oil was recrystallized from heptane[4] to give 0.75 g., (20.3%), needles, m.p. 102–105°, shown to be *2-(2-naphthoxy)-1-p-nitrophenylethanol* (IV) by reduction and deamination, as before, to the known 2-(2-naphthoxy)-1-phenylethanol (2), m.p. 85–86°. The analytical sample melted at 106–107°.

Anal. Calc'd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53.
Found: C, 70.06; H, 4.77; N, 4.78.

No other product could be isolated from this alkali-insoluble fraction of the reaction mixture.

The alkaline extract, containing the alkali-soluble products of the reaction, was now acidified with dil. hydrochloric acid and extracted with benzene, which was washed with water and dried over magnesium sulfate. When removal of the benzene left an unpromising

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[4] The heptane referred to here and elsewhere in this paper is Eastman's mixture of C_7 hydrocarbons (P 2215).

residue, the mixture was redissolved in benzene (75 ml.), *p*-toluenesulfonic acid (0.1 g.) was added, and the solution was refluxed for three hours. The benzene solution then was extracted with 4% sodium hydroxide and the benzene was evaporated. The dark brown residue again was dissolved in benzene, passed through an alumina column, and the solvent was removed. Recrystallization of the residue from absolute ethanol gave 0.75 g. (21.4%) of the dihydrofuran (II), m.p. 126–127°. Over 92% of the excess 2-naphthol used in the reaction also was recovered, but no other reaction product could be isolated in a pure state.

p-Methoxystyrene oxide and 2-naphthol, acid-catalyzed. In an appropriate apparatus, heated in an oil-bath at 120°, was placed 2-naphthol (11.7 g., 0.081 mole) and *p*-toluenesulfonic acid (0.1 g.). To this was added *p*-methoxystyrene oxide (6) (3.7 g., 0.025 mole). The one-phase mixture was immediately cooled to 100° and maintained at this temperature for 15 minutes. Benzene (250 ml.) was use to dissolve the reaction mixture which then was extracted with 4% sodium hydroxide (250 ml.) to remove alkali-soluble components. The benzene solution was washed with water and the benzene was removed to leave a brown oil. This oil, in benzene, was passed through an alumina column. Removal of the solvent left an oil that solidified on warming and stirring with ethanol. The solid was recrystallized from glacial acetic acid, 1.2 g. (11.9%), needles, m.p. 171–172°. The analyses corresponded to that calculated for *14-p-methoxybenzyl-14H-dibenzo*[*a,j*]*xanthene*, a type of compound often encountered at this point in acid-catalyzed reactions of other oxides with 2-naphthol. No structure proof was undertaken.

Anal. Calc'd for $C_{29}H_{22}O_2$: C, 86.54; H, 5.51.
Found: C, 86.46; H, 5.81.

No other pure compound was isolated from this reaction mixture.

p-Methoxystyrene oxide and sodium 2-naphthoxide. A mixture of 2-naphthol (6.5 g., 0.045 mole) in sodium hydroxide (0.6 g., 0.015 mole) and water (6 ml.) in a three-necked flask was heated in a boiling water-bath. To this mixture was added *p*-methoxystyrene oxide (2.25 g., 0.015 mole) with stirring and with nitrogen flowing through the system. After 20 minutes the one-phase mixture was taken up in benzene (250 ml.) and extracted with 4% sodium hydroxide (250 ml.). Removal of the benzene left a pale, brown oil that partially solidified when stirred with heptane. The material was heated in heptane, the oil allowed to settle, and the clear, supernatant solution then was decanted and allowed to cool. The crystals so obtained were filtered and the heptane treatment was repeated, using the filtrate for this purpose. A total of 1.35 g. (30.7%), needles, m.p. 87–92° thus was obtained. This material was proved to be *2-(2-naphthoxy)-2-p-methoxyphenylethanol* (V). The analytical sample melted at 91–92°.

Anal. Calc'd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16.
Found: C, 77.31; H, 6.33.

The foregoing alkaline extract that contained the alkali-soluble portion of the reaction mixture was acidified with dil. hydrochloric acid and extracted with benzene. Instead of trying to isolate the expected phenolaclohol (VI), the benzene solution, after the addition of *p*-toluenesulfonic acid (0.1 g.), was refluxed three hours to convert any of the phenol-alcohol (VI) to the furan (VII). The benzene solution then was washed with 4% sodium hydroxide and the benzene was removed. This left an oil that soon solidified. Recrystallization from heptane gave 1.63 g. (39.4%), of needles, m.p. 102–104°, shown to be *1-p-methoxyphenyl-1,2-dihydronaphtho*[*2,1-b*]*furan* (VII). The analytical sample melted at 104.5–105.5°.

Anal. Calc'd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84.
Found: C, 82.46; H, 5.71.

It was interesting to observe that the first time this furan was obtained, it melted at 77–78° and gave correct analytical values. After the lower-melting form had stood for awhile, its melting point changed to 104–105°, and thereafter all preparations of the furan exhibited the higher melting point. This phenomenon, originally observed in Los Angeles, was later duplicated in Fort Collins.

Styrene oxide and sodium 1-naphthoxide. To a stirred mixture of 1-naphthol (21.6 g., 0.15 mole) in sodium hydroxide (2 g., 0.05 mole) and water (8 ml.), heated in a boiling water-bath, was added styrene oxide (6.0 g., 0.05 mole) over a period of 15 minutes. After an additional 45 minutes, the mixture was taken up in benzene (200 ml.) and extracted with 4% sodium hydroxide (200 ml.); the alkaline solution was saved. The benzene solution was washed with water and the benzene was removed to obtain 4.0 g (30.3%), assumed to be a mixture of VIII and IX, as a brown oil.

This oil was added to a solution of phthalic anhydride (3.0 g.), pyridine (3 ml.), and dioxane (15 ml.) and allowed to stand at room temperature for four hours in order to esterify the primary alcohol but not the secondary alcohol. The solution then was taken up in ether (100 ml.), washed with dil. hydrochloric acid (5 ml. of conc'd acid in 50 ml. of water), and finally with water (50 ml.). Then the ether solution was extracted with four 50-ml. portions of 5% sodium bicarbonate, the extract being reserved. The ether solution was dried over potassium carbonate and the ether was removed under reduced pressure to leave 0.7 g. (5.3%) of an oil. This oil was dissolved in hot heptane, the solution was cooled to room temperature, and the supernatant liquid was separated and cooled further. In this manner 0.3 g. (2.3%) of a solid, m.p. 95–100° was isolated. Further purification and alternative synthesis showed this compound to be *2-(1-naphthoxy)-1-phenylethanol* (IX), m.p. 102.5–103.5°.

Anal. Calc'd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10.
Found: C, 82.00; H, 6.28.

The foregoing bicarbonate extract of the esterification mixture was treated with sodium hydroxide (4 g.) in water (10 ml.) and heated one hour. The oil that separated was taken up in ether, dried over potassium carbonate, and evaporated to leave 1.8 g. (13.6%) oil. This oil was converted to a *p*-nitrobenzoate, 2.0 g. (9.7% based on the oxide), m.p. 50–110°, and finally 1.2 g. (5.8%), m.p. 117–119° after further purification. The mixture melting point with the pure *p*-nitrobenzoate of 2-(1-naphthoxy)-2-phenylethanol (VIII), m.p. 119–120°, was 118–120°.

The 4% sodium hydroxide extract of the original oxide-1-naphthol reaction mixture was acidified with dil. hydrochloric acid and extracted with benzene. Removal of the benzene left 23.5 g. of a brown oil. This oil was redissolved in benzene (75 ml.) and *p*-toluenesulfonic acid (0.1 g.) was added. After a four-hour reflux period, the solution was extracted with 4% sodium hydroxide, the extract being saved. The benzene solution was washed with water and the benzene was removed to leave 6.0 g. of oil which, in benzene, was passed through an alumina column. Subsequent removal of the solvent left 3.8 g. of colorless oil that solidified on standing. Recrystallization from heptane gave 3.5 g. (28.5%), m.p. 75–76°. Further purification raised the melting point to 77–78°; this material was shown by mixture melting point to be identical with the available (13) 3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan derivable from XI by cyclization.

The alkaline extract from the cyclization step was acidified with dil. hydrochloric acid and extracted with benzene. Removal of the solvent left 16.5 g. of brown solid. This was heated with benzene, and Skellysolve C was added to cloudiness. The material obtained on cooling was subjected to repeated recrystallization from benzene to obtain 1.2 g. (9.1%) of platelets, m.p. 183–185°. The analytical sample of this material, shown hereafter to be *2-(4-hydroxy-1-naphthyl)-2-phenylethanol* (X), melted at 186–187°.

Anal. Calc'd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10.
Found: C, 81.70; H, 6.23.

For structure proof, this phenolalcohol (1 g.) was dissolved in 10% sodium hydroxide and small portions of diethyl sulfate were added thereto, along with additional sodium hydroxide to maintain alkalinity. The oil that separated was extracted with benzene, washed with water and the benzene was removed. Recrystallization of the residual oil from heptane gave 0.38 g. (34.5%) of 2-(4-ethoxy-1-naphthyl)-2-phenylethanol, m.p. 87–88°, which compound was synthesized by another method.

Cyclohexene oxide and sodium 2-naphthoxide. A solution of 2-naphthol (21.6 g., 0.15 mole) in sodium hydroxide (6.0 g., 0.15 mole) and water (40 ml.) was stirred and heated in a boiling water-bath while cyclohexene oxide (4.9 g., 0.05 mole) was added in 15 minutes. A heavy precipitate made it necessary to add more water (20 ml.) to facilitate stirring. After an additional 35 minutes, the mixture was cooled, filtered, and the precipitate was washed free of sodium 2-naphthoxide. The dried product was practically pure, 10.5 g. (86.8%), m.p. 134–135°. Normally this mode of ring opening leads to the *trans* form. The analytical sample of this *2-(2-naphthoxy)-cyclohexanol* (XII) melted at 134.5–135.5°, from heptane.

Anal. Calc'd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49.

Found: C, 79.05; H, 7.28.

The *p-nitrobenzoate* melted at 104.5–105.5°.

Anal. Calc'd for $C_{23}H_{21}NO_5$: C, 70.57; H, 5.41; N, 3.58.

Found: C, 71.01; H, 5.33; N, 3.72.

Acidification of the alkaline filtrate from the reaction mixture gave a 96.5% recovery of the excess 2-naphthol, m.p. 119–120° without any purification, indicating the absence of any alkali-soluble contaminants from the reaction.

Cyclohexene oxide and 2-naphthol, acid-catalyzed. Cyclohexene oxide (9.8 g., 0.1 mole) was added to a stirred mixture of 2-naphthol (43.2 g., 0.3 mole) and *p*-toluenesulfonic acid (0.1 g.) at 140°. After two hours at this temperature the one-phase mixture was dissolved in carbon tetrachloride (250 ml.) and extracted with 4% sodium hydroxide (250 ml.). The carbon tetrachloride solution was dried over magnesium sulfate before removing the solvent, leaving 23.0 g. of a partially solid, tan residue. Recrystallization from heptane gave 4.6 g. (19%) of 2-(2-naphthoxy)-cyclohexanol (XII), m.p. 134–135°.

The remainder of the product in the heptane solution was adsorbed on an alumina column and was fractionally eluted. The first fraction, eluted with heptane and a heptane-benzene mixture, formed a red picrate, 1.8 g., m.p. 106–110°. Decomposition of this picrate in benzene on a alumina column gave a white solid that was purified by recrystallization from heptane, 0.7 g. (3.1%), needles, m.p. 56–57.5°. It showed no evidence of unsaturation when treated with bromine in carbon tetrachloride. Analysis agreed with that required for 7a,8,9,10,11, 11a-hexahydrobenzo[*d*]naphtho[2,1-*b*]furan (XV).

Anal. Calc'd for $C_{16}H_{16}O$: C, 85.67; H, 7.19.

Found: C, 85.44; H, 7.20.

Further elution of the alumina column with benzene gave a colorless oil that solidified on standing, 2.5 g., m.p. 142–150°. By fractional crystallization from heptane this material was further separated into two components, or, preferably, by passing a benzene-heptane solution through another alumina column, using heptane and benzene as eluants. A material melting at 156° was less strongly adsorbed. In this manner, 1.3 g. (3.7%), m.p. 156–157° and 0.5 g. (2.2%), m.p. 191–192° were isolated. For the compound melting at 156–157°, analyses and molecular weight value suggested the structure, 14,14-pentamethylene-14*H*-dibenzo[*a,j*]xanthene (XIV).

Anal. Calc'd for $C_{26}H_{22}O$: C, 89.11; H, 6.33; Mol. Wt., 350.

Found: C, 89.15; H, 6.34; Mol. Wt. (Rast camphor) 328.

It was found that a mixture of the etheralcohol (XII) (5.0 g., 0.02 mole) and 2-naphthol (5.8 g., 0.04 mole) with *p*-toluenesulfonic acid (0.1 g.), heated at 150° for three hours, produced this presumed xanthene (XIV), 1.3 g. (18.6%). Attempts to prepare this xanthene from cyclohexanone and 2-naphthol were unsuccessful. As for the 191–192°-melting compound, the analyses and molecular weight agreed with that calculated for 2,2′-di-(2-naphthoxy)-dicyclohexyl ether (XVI).

Anal. Calc'd for $C_{32}H_{34}O_3$: C, 82.37; H, 7.34; Mol. Wt., 467.

Found: C, 82.33; H, 7.60; Mol. Wt. (Rast camphor) 446.

Further elution of the column with benzene and a benzene-chloroform mixture removed a product that formed an orange-yellow picrate, 2.6 g., m.p. 143–145°. Decomposition of the picrate in benzene on an alumina column and elution with chloroform gave 1.4 g. (8.2%) of a solid that was recrystallized from heptane, m.p. 106–107°. To this has been assigned the structure 2-(2-naphthoxy)-2′-hydroxydicyclohexyl ether (XIII).

Anal. Calc'd for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29.

Found: C, 77.39; H, 8.14.

This compound also was obtained by treatment of the etheralcohol (XII) with an excess of cyclohexene oxide in the presence of *p*-toluenesulfonic acid under the conditions of the original reaction. The picrates from both sources showed no depression in melting point.

Further elution of the column with chloroform and methanol gave 0.6 g., m.p. 134–135° of the etheralcohol (XII), making a total of 5.2 g. (21.5%) of this compound.

Synthesis of 2-(2-naphthoxy)-2-p-methoxyphenylethanol (V). The reaction of ethyl α-hydroxy-*p*-methoxyphenylacetate (14) with phosphorus oxychloride (15) was used to prepare ethyl α-chloro-*p*-methoxyphenylacetate, b.p. 125–127°/1 mm., n_D^{20} 1.5248; literature (16) b.p. 175°/20 mm.

This ester (6.6 g., 0.029 mole) in absolute ethanol was added dropwise to a refluxing solution of 2-naphthol (8.4 g., 0.058 mole) in ethanolic sodium ethoxide prepared from sodium (1.3 g., 0.058 g.-atom) in absolute ethanol (30 ml.). After four hours the mixture was cooled, filtered, and the insoluble material was washed with absolute ethanol. This solid was dissolved in water and acidified with dil. hydrochloric acid. The product, *α-(2-naphthoxy)-p-methoxyphenylacetic acid*, was recrystallized from heptane, 1.3 g. (14.5%), needles, m.p. 145.5–146.5°.

Anal. Calc'd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23.
Found: C, 74.04; H, 5.36.

The acid was reduced with lithium aluminum hydride in tetrahydrofuran to give a 48.8% yield of product, m.p. 91–92° alone or when mixed with V from the reaction of *p*-methoxystyrene oxide with sodium 2-naphthoxide.

Synthesis of 1-p-methoxyphenyl-1,2-dihydronaphtho[2,1-b]-furan (VII). The lactone of α-(2-hydroxy-1-naphthyl)-*p*-methoxyphenylacetic acid (1.2 g., 0.004 mole, m.p. 143–145°), prepared by the method of Bistrzycki (17), was added to lithium aluminum hydride (0.5 g., 0.013 mole) in dry ether (50 ml.). The mixture was warmed on the steam-bath for two hours and then was worked up in the usual manner. The product was recrystallized from ethanol, 0.93 g. (77.5%), m.p. 129.5–130.5°. This was *2-(2-hydroxy-1-naphthyl)-2-p-methoxyphenylethanol* (VI), the phenolalcohol assumed to be present in the reaction mixture from *p*-methoxystyrene oxide and sodium 2-naphthoxide.

Anal. Calc'd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16.
Found: C, 77.27; H, 5.97.

A solution of this phenolalcohol (VI) (0.8 g.) in benzene (50 ml.) containing *p*-toluenesulfonic acid (0.1 g.) was refluxed two hours. The cooled benzene solution was passed through an alumina column, the benzene was removed and the residual oil was recrystallized from heptane to obtain 0.64 g. (86%) of needles, m.p. 104–105° alone or when mixed with VII from the *p*-methoxystyrene oxide-sodium 2-naphthoxide reaction product.

Synthesis of 2-(1-naphthoxy)-2-phenylethanol (VIII). Sodium (2.3 g., 0.1 g.-atom) was interacted with absolute ethanol (60 ml.) and to this solution was added 1-naphthol (14.4 g., 0.1 mole). To this mixture was added ethyl α-bromophenylacetate (12.2 g., 0.05 mole, n_D^{20} 1.5385) in absolute ethanol (100 ml.). A precipitate formed immediately. The mixture was warmed to 50°, allowed to stand one hour, filtered, the precipitate was washed with absolute ethanol, and the filtrate and washing were diluted with water. The insoluble layer was taken up in ether, the ether was evaporated, and the residue was hydrolyzed with sodium hydroxide in dilute ethanol by refluxing five hours. Water and Dry Ice were added to the cooled reaction mixture to separate the excess 1-naphthol, which was taken up in ether. Acidification of the aqueous layer gave an oil that soon solidified, 11.3 g. (81.3%). Purifying recrystallizations from benzene and then from dilute ethanol gave 5.3 g. of *α-(1-naphthoxy)-phenylacetic acid*, m.p. 167–168.5°.

Anal. Calc'd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07.
Found: C, 77.38; H, 4.89.

The *anilide*, from dil. ethanol, melted at 144–145°.

Anal. Calc'd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42.
Found: C, 81.50; H, 5.85.

This acid (2.78 g., 0.01 mole) was reduced with lithium aluminum hydride (0.5 g.) in ether in the usual manner in a quantitative yield and the product was distilled at 180–185°/2 mm. The product, *2-(1-naphthoxy)-2-phenylethanol* (VIII), gave the correct analyses but remained as a viscous oil for several weeks. Eventually it solidified, m.p. 78.5–80°.

Anal. Calc'd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10.

Found: C, 81.62; H, 5.83.

The p-nitrobenzoate, from dil. ethanol, melted at 119–120°.

Anal. Calc'd for $C_{25}H_{19}NO_5$: C, 72.63; H, 4.63.

Found: C, 72.49; H, 4.28.

Synthesis of 2-(1-naphthoxy)-1-phenylethanol (IX). To a solution of sodium hydroxide (8 g., 0.2 mole) in water (100 ml.) and dioxane (100 ml.) was added 1-naphthol (28.8 g., 0.2 mole) and, finally, phenacyl bromide (38.8 g., 0.195 mole). This mixture, with stirring, was heated to its boiling point and then was allowed to cool before it was poured into an ice-water slurry. The insoluble oil was reluctant to crystallize, so it was taken up in ether, dried over sodium sulfate, and then was distilled to obtain 30.5 g. (60%), b.p. 220–230°/6 mm. This distillate readily solidified and was recrystallized from ethanol as needles, m.p. 70–71°, which, by their method of preparation, were assumed to be *α-1-naphthoxyacetophenone.* Knott (18) has prepared this compound by the same reaction and has reported m.p. 59°.

Anal. Calc'd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38.

Found: C, 82.60; H, 5.41.

The *2,4-dinitrophenylhydrazone,* from ethyl acetate as orange needles, melted at 206–207°.

Anal. Calc'd for $C_{24}H_{18}N_4O_5$: C, 65.15; H, 4.10.

Found: C, 65.00; H, 4.36.

The α-1-naphthoxyacetophenone (5.2 g., 0.02 mole) was reduced with lithium aluminum hydride (0.5 g.) in ether in the usual manner to obtain 4.9 g. (92.5%), m.p. 95–103°, which, when recrystallized from heptane, gave coarse needles, m.p. 102.5–103.5°, identical with IX from the oxide-1-naphthol reaction as shown by a mixture melting point.

The *p-nitrobenzoate,* from ethanol, melted at 157–158°.

Anal. Calc'd for $C_{25}H_{19}NO_5$: C, 72.63; H, 4.63.

Found: C, 72.80; H, 4.74.

Synthesis of 2-(4-ethoxy-1-naphthyl)-2-phenylethanol. An ether solution of 4-ethoxy-1-benzoylnaphthalene (36.0 g., 0.13 mole), prepared from ethyl 1-naphthyl ether (19) by the method of Scholl and Seer (20), was added to lithium aluminum hydride (1.8 g., 0.048 mole) in anhydrous ether over a 20-minute period. After an additional ten minutes the mixture was decomposed with dilute acid, extracted with ether, dried over sodium sulfate, and the ether was removed. The colorless residual oil, 32.5 g. (90%), was used without further purification.

The foregoing carbinol was refluxed ten minutes with 48% hydrobromic acid (150 ml.) after which time the upper oily layer was converted to a yellow solid. This solid was filtered, washed with water, and dried under a vacuum. Several recrystallizations from petroleum ether gave 32.0 g. (78%), m.p. 123–124°, of *α-(4-ethoxy-1-naphthyl)benzyl bromide.*

Anal. Calc'd for $C_{19}H_{17}BrO$; C, 66.87; H, 5.02.

Found: C, 66.83; H, 4.72.

A mixture of the substituted benzyl bromide (5.0 g., 0.015 mole) and mercuric cyanide (10.0 g., 0.04 mole) was heated in an oil-bath to 165° and held at this temperature for five minutes. The oil from the cooled mixture was dissolved in benzene, filtered, passed through an alumina column, and the benzene was removed, leaving 3.1 g. (72.1%) of solid which was recrystallized from heptane. This *α-(4-ethoxy-1-naphthyl)phenylacetonitrile,* needles, melted at 128–129°.

Anal. Calc'd for $C_{20}H_{17}NO$: C, 83.59; H, 5.96.

Found: C, 83.47; H, 5.89.

The nitrile could be hydrolyzed only as far as the amide by ordinary methods. However, when the nitrile (3.0 g., 0.01 mole) was added to ethylene glycol (25 ml.) containing sodium hydroxide (1.2 g.) and water (6 ml.) and the mixture was refluxed for 36 hours, complete hydrolysis was effected. The reaction mixture afforded 2.1 g. (68.6%) *α-(4-ethoxy-1-naphthyl)phenylacetic acid*, m.p. 185–186°, from dilute ethanol.

Anal. Calc'd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92.
Found: C, 78.58; H, 5.98.

The acid (1.7 g., 0.0055 mole) was added to lithium aluminum hydride (0.6 g., 0.016 mole) in dioxane (100 ml.) but no reaction occurred unless the mixture was warmed. The reduction product was isolated in the usual manner, was recrystallized from heptane, 0.75 g. (46.9%), m.p. 87–88°, and was *2-(4-ethoxy-1-naphthyl)-2-phenylethanol.*

Anal. Calc'd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90.
Found: C, 82.16; H, 6.98.

A mixture melting point determination confirmed the identity of this compound with that derived from X.

SUMMARY

p-Nitrostyrene oxide, *p*-methoxystyrene oxide, and cyxlohexene oxide were interacted with 2-naphthol, acid-catalyzed, and with aqueous sodium 2-naphthoxide. The substituted styrene oxides resembled styrene oxide itself in the type of products formed. Cyclohexene oxide, on the other hand, was similar to propylene oxide in that no nuclear attack to give a phenolalcohol was evident. Four products from the reaction of styrene oxide with aqueous sodium 1-naphthoxide were identified.

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