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

The Reaction of *trans*-Stilbene Oxide and 1,1-Diphenylethylene Oxide with 2-Naphthol

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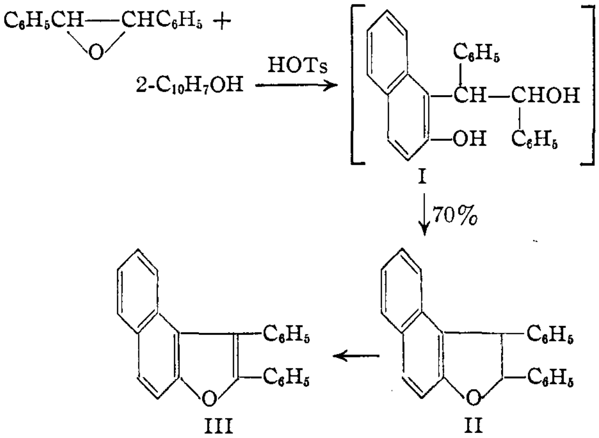
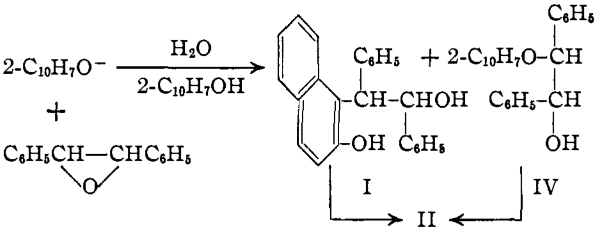
trans-Stilbene oxide and 2-naphthol interacted rapidly when acid catalyzed to give 1,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan. These reactants, in an alkaline medium, slowly formed an ether-alcohol and a phenol-alcohol both of which could be cyclized to the aforementioned furan. 1,1-Diphenylethylene oxide and 2-naphthol in alkaline medium formed a phenol-alcohol, but with acid catalysis the oxide rearranged to diphenylacetaldehyde prior to reaction with 2-naphthol. These results are discussed in terms of ring-opening mechanisms.

The present investigation was undertaken as an extension of our study of the ring-opening reactions of olefin oxides, particularly styrene oxides.[3] *trans*-Stilbene oxide and 1,1-diphenylethylene oxide were selected because of their relationship to styrene oxide and their ready availability. As a co-reactant 2-naphthol was chosen instead of phenol because the former is more susceptible to electrophilic attack than the latter. The incidence of nuclear attack in the reaction between an oxide and a phenol was a point of interest.

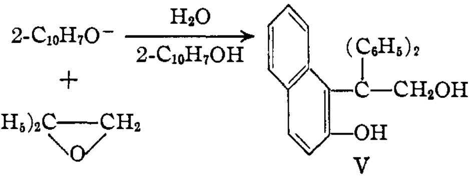
The acid-catalyzed reaction of *trans*-stilbene oxide with 2-naphthol, at 105–120°, proceeded as shown. Presumably a phenol-alcohol was first formed and then cyclized under these reaction conditions to the dihydrofuran II. That the phenol-alcohol I was not necessarily the intermediate, however, is shown later. Proof of the structure of the dihydrofuran II consisted in its dehydrogenation, both with sulfur and with NBS, to the known 1,2-diphenylnaphtho[2,1-b]furan (III).

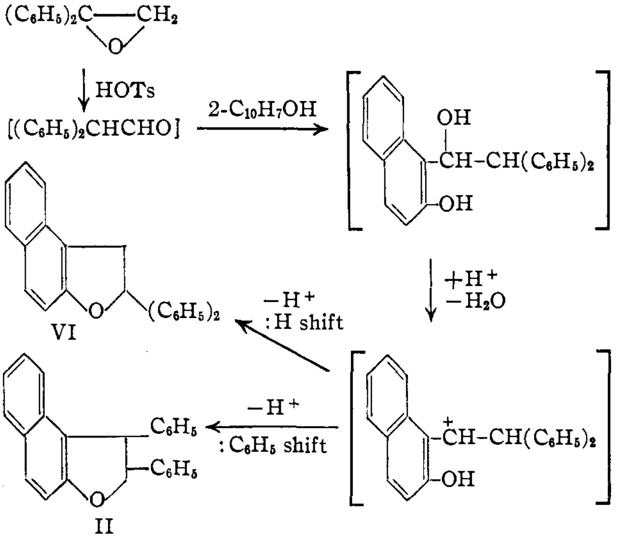


The relatively slow reaction of *trans*-stilbene oxide with 2-naphthol in alkaline medium gave two products: the ether-alcohol IV (46.5%) and the phenol-alcohol I (14.7–22.4%). Both IV and I could be cyclized to the dihydrofuran II, which constituted additional evidence for the structure assigned to II. The cyclization of IV to II precludes the inevitability, but not the probability, of I as an intermediate in the acid-catalyzed reaction of the oxide with 2-naphthol. Formation of the phenol-alcohol I by way of the rearrangement of the ether-alcohol IV was unlikely in alkaline medium but could have occurred during the acid-catalyzed cyclization of IV to the furan II.[3c]



The reaction of 1,1-diphenylethylene oxide with 2-naphthoxide ion gave the known phenol-alcohol V in 15.4% yield. Unfortunately no other pure reaction product was isolated.





Acid catalysis of the reaction of 1,1-diphenylethylene oxide with 2-naphthol appeared to give only two products, both alkali insoluble. One (59%) was identical with the dihydrofuran II obtained from *trans*-stilbene oxide and 2-naphthol; the other (20.2%) was either the *cis* or *trans* isomer of II or 2,2-diphenyl-1,2-dihydronaphtho[2,1-b]-

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

[3] (a) C. O. Guss, THIS JOURNAL, **71**, 3460 (1949); (b) C. O. Guss and L. H. Jules, *ibid.*, **72**, 3878 (1950); (c) C. O. Guss, H. R. Williams and L. H. Jules, *ibid.*, **73**, 1257 (1951); (d) C. O. Guss and H. G. Mautner, *J. Org. Chem.*, **16**, 887 (1951); (e) C. O. Guss and H. R. Williams, *ibid.*, **16**, 1809 (1951); (f) C. O. Guss, *ibid.*, **17**, 678 (1952); (g) C. O. Guss, THIS JOURNAL, **74**, 2561 (1952).

furan (VI) since it was isomeric with II but was not the known 1,1-diphenyldihydronaphthofuran derivable from V. Buttenberg[4] had obtained a compound from the acid-catalyzed reaction of diphenylacetaldehyde and 2-naphthol which was reported to melt at 141–142° and to which either structure VI or the 1,1-isomer of VI was assigned. The latter structure was excluded when 1,1-diphenyl-1,2-dihydronaphtho[2,1-b]furan was recently prepared and found to melt at 172–174°.[5] Since our compound assigned structure II melted at 140.5–141.5°, Buttenberg's synthesis was repeated and the identity of his compound and our structure II thus demonstrated, making a previous conjecture regarding the structure of Buttenberg's compound erroneous.[5]

If the oxide isomerized to diphenylacetaldehyde[6] before reaction with 2-naphthol occurred, it is necessary to postulate rearrangement in the ion shown with a shift of either a phenyl or a hydrogen before cyclization to II or VI. On the other hand, if the oxide reacted at the α-carbon (assuming a first-order ring opening) with 2-naphthol to give either an ether-alcohol or the phenol-alcohol V, then the former could cyclize easily to VI without undergoing rearrangement, while the latter should close to give the 1,1-isomer of VI. In order to explain the formation of II by this scheme, the phenol-alcohol V must rearrange with shifts of phenyl and hydrogen before ring closure. Since II is the major product, it would be strange if none of the 1,1-isomer of VI were formed if the oxide attack at the α-carbon of the oxide was the predominant path. On the other hand, if the oxide first rearranged to the aldehyde, the reaction scheme shown is such as to predict a preponderance of II over VI in line with the known tendency of phenyl to shift in preference to hydrogen.

Styrene oxide, and several substituted styrene oxides, have been found[3] to react with phenol and with 2-naphthol to give phenol-alcohols (primary) as well as ether-alcohols (principally primary except with the nitrostyrene oxides). The relative amounts of the two types of products (phenol or ether) depended on the oxide, the phenol and the reaction conditions employed. Boyd and Marle[7] have found that the reaction of ethylene oxide and of propylene oxide with 2-naphthol in alkaline medium gave ether-alcohols in nearly quantitative yield. The reaction of styrene oxides to give primary alcohols, that is, nucleophilic attack on the oxide at the α-C-atom, has been considered to be a unimolecular reaction, and certain evidence has been cited in support of this postulate.[3d,e,f,g] Those oxides which, under favorable conditions, would most likely follow a unimolecular ring-opening mechanism also give phenol-alcohols in their reactions with phenols, and, conversely, oxides, such as ethylene oxide and propylene oxide, which are not as susceptible to a unimolecular mechanism, give only ether-alcohols (a secondary alcohol[8] from propylene oxide). This suggests that nuclear attack on a phenol might be diagnostic of a unimolecular ring opening by the oxide. Such an interpretation, when applied to the results from the reaction of *trans*-stilbene oxide with 2-naphthol, indicates that a certain amount of unimolecular ring opening occurred in alkaline medium and was probably dominant in the acid-catalyzed reaction.

1,1-Diphenylethylene oxide would be expected to be quite resistant to a bimolecular attack at the α-C-atom by the 1-position of the 2-naphthol because of steric factors. The fact that the phenol-alcohol V was isolated is a good indication that steric factors do not strongly inhibit the reaction, a behavior in harmony with a unimolecular mechanism.

It is pertinent to point out that styrene oxide and 1,1-diphenylethylene oxide are both opened at the β-C-atom in their reaction with phenyllithium under conditions unfavorable for the operation of a unimolecular ring opening.[9]

Experimental[10]

Acid-catalyzed Reaction of *trans*-Stilbene Oxide with 2-Naphthol.—In a suitable reaction flask 2-naphthol (4.3 g., 0.03 mole) was completely melted by heating to 140° and then cooled to 120°. To this stirred liquid was added, respectively, *p*-toluenesulfonic acid monohydrate (0.1 g.) and *trans*-stilbene oxide (2.0 g., 0.01 mole, m.p. 69–70°, prepared by the method of Böeseken and Elsen[11]). The dark red, one-phase reaction mixture was immediately cooled to 105° and stirred for 15 minutes at this temperature. Dissolution of the cooled mixture in benzene (250 cc.) and extraction with 4% sodium hydroxide (250 cc.) removed unreacted 2-naphthol, of which 93% of the excess was recovered. Evaporation of the benzene left a residue that was digested with hot methanol and then cooled to give 2.25 g. (69.9%) of light pink solid, m.p. 135–137°, shown to be **1,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan** (II). The analytical sample, from glacial acetic acid, melted at 140.5–141.5°.

Anal. Calcd. for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.62; H, 5.57.

No other pure compounds were isolated from the reaction mixture although attempts were made to do so.

The assignment of structure followed dehydrogenation of the dihydrofuran to the known 1,2-diphenylnaphtho[2,1-b]furan (III).[12] Thus, the dihydrofuran II (1.5 g.) and sulfur (0.15 g.) were heated together at 280–300° for 3 hours with accompanying hydrogen sulfide liberation. The product was purified by sublimation at 200–230° (1 mm.) and the oily sublimate then crystallized from dilute acetic acid and several times from dilute methanol, m.p. 103–104°.

Anal. Calcd. for $C_{24}H_{16}O$: C, 89.97; H, 5.03. Found: C, 90.10; H, 5.30.

The authentic 1,2-diphenylnaphtho[2,1-b]furan, reported to melt at 106°,[12] was also prepared by the literature method.[12] A mixed melting point confirmed the identity of the two compounds.

Dehydrogenation by means of the reaction with N-bromosuccinimide also yielded III. When the dihydrofuran II (1.0 g.) and NBS (0.6 g.) in carbon tetrachloride (25 cc.) and a small amount of benzoyl peroxide were heated at reflux, a reddish-orange color rapidly appeared and then faded to colorless. Hydrogen bromide evolution was copious. After 10 minutes, the succinimide was filtered from the cooled mixture, solvent was evaporated, and the residue refluxed with anhydrous potassium acetate (1.3 g.) in glacial acetic acid (25 cc.) for 3 hours. The product was purified by sublimation and recrystallization from dilute methanol to obtain a small yield of III.

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(4) W. Buttenberg, *Ann.*, **279**, 333 (1894).

(5) C. O. Guss, THIS JOURNAL, **73**, 608 (1951).

(6) A. Klages and J. Kessler, *Ber.*, **39**, 1753 (1906).

(7) D. Boyd and E. Marle, *J. Chem. Soc.*, **105**, 2117 (1914).

(8) C. D. Hurd and P. Perletz, THIS JOURNAL, **68**, 38 (1946).

(9) S. J. Cristol, J. R. Douglass and J. S. Meek, *ibid.*, **73**, 810 (1951).

(10) All temperature measurements are uncorrected. Microanalyses by Mr. Joseph Pirie of this Department.

(11) J. Böeseken and G. Elsen, *Rec. trav. chim.*, **47**, 694 (1928).

(12) O. Dischendorfer and E. Ofenheimer, *Monatsh.*, **74**, 135 (1943).

Reaction of *trans*-Stilbene Oxide with 2-Naphthoxide Ion.—A solution of 2-naphthol (4.3 g., 0.03 mole), sodium hydroxide (0.4 g., 0.01 mole) and water (5 cc.) was placed in an apparatus arranged for stirring, heating and condensing. While this mixture was maintained under nitrogen and heated in a boiling water-bath, *trans*-stilbene oxide (2.0 g., 0.01 mole) was added. After 28 hours the one-phase mixture was cooled somewhat, taken up in benzene (200 cc.) and the warm solution extracted with 4% sodium hydroxide (200 cc.). Removal of the benzene left a solid which was crystallized from heptane, 1.6 g. (46.5%). The pure, white needles (41.2%), m.p. 118.5–119.5°, was considered to be **2-(2-naphthoxy)-1,2-diphenylethanol** (IV), a deduction based on the mode of formation, alkali insolubility, the analysis and the formation of a urethan.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.97; H, 5.98.

The phenylurethan melted at 163–164°.

Anal. Calcd. for $C_{31}H_{25}NO_3$: N, 3.05. Found: N, 2.83.

When a solution of this ether-alcohol IV in benzene containing a small amount of *p*-toluenesulfonic acid monohydrate was refluxed 3 hours, a 75% yield of the cyclized product, 1,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan (II) was obtained.

The alkali-soluble fraction from the reaction of the oxide with 2-naphthol was worked up with and without isolation of the phenol-alcohol I present. Since the expected phenol-alcohol I was presumed to exhibit less solubility in alkali than would 2-naphthol, a separation of the two was attempted as follows. The alkaline solution of the alkali-soluble materials from the reaction was acidified with dilute hydrochloric acid and then extracted with benzene (300 cc.). This benzene solution was now extracted with cold 4% sodium hydroxide (250 cc.) to remove excess 2-naphthol. Evaporation of the benzene left 0.8 g. of a light brown oil, which was fractionally recrystallized from heptane to give 0.5 g. (14.7%), white needles, m.p. 151–152°. This product was apparently **2-(2-hydroxy-1-naphthyl)-1,2-diphenylethanol** (I). A 96.5% recovery of excess 2-naphthol was realized.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.53; H, 5.66.

The phenol-alcohol I was cyclized, by refluxing a solution in benzene containing *p*-toluenesulfonic acid monohydrate, to the dihydrofuran II in 67.8% yield, a result in agreement with the structure assigned to II.

An alternate method for working up the alkali-soluble fraction from the oxide–naphthol reaction consisted in acidification of the alkaline solution of the alkali solubles with dilute hydrochloric acid, followed by benzene extraction. The benzene solution, after addition of a small amount of *p*-toluenesulfonic acid monohydrate, was refluxed 3 hours, extracted with 4% sodium hydroxide, washed with water, dried and then passed through a column filled with activated alumina (30 × 1 cm.). Removal of the benzene and crystallization of the residue from ethanol and then from glacial acetic acid gave 0.72 g. (22.4%) of 1,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan (II).

It is perhaps worthwhile noting that *trans*-stilbene oxide was relatively low in reactivity in this reaction. A reaction time of 4 hours gave only a 20.6% yield of the ether-alcohol IV and a 12.5% yield of the dihydrofuran II; a reaction time of 1 hour permitted a nearly quantitative recovery of unreacted oxide.

Acid-catalyzed Reaction of 1,1-Diphenylethylene Oxide with 2-Naphthol.—To a mixture of 2-naphthol (4.3 g., 0.03 mole) and *p*-toluenesulfonic acid monohydrate (0.1 g.) at 120° was added 1,1-diphenylethylene oxide (2.0 g., 0.01 mole, m.p. 55–56°, prepared by the method of Klages and Kessler[6]). This mixture was immediately cooled to 100° and maintained at this temperature for 15 minutes. The cooled mixture was then taken up in benzene (200 cc.) and extracted with 4% sodium hydroxide (200 cc.). After the benzene solution was washed with water, removal of the benzene under reduced pressure left a pale yellow oil which solidified when stirred with ethanol. Recrystallization from absolute ethanol gave 1.9 g. (59.0%) of white needles, m.p. 140.5–141.5°. A mixed melting point and analysis indicated that this compound was identical with that obtained from the acid-catalyzed reaction of *trans*-stilbene oxide with 2-naphthol, namely, 1,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan (II).

The mother liquor from the foregoing recrystallization was freed of ethanol under reduced pressure, and the resulting oil was dissolved in benzene and passed through an alumina column (20 × 1 cm.). Removal of the benzene left an oil which was warmed in absolute ethanol and slowly cooled to give 0.65 g. (20.2%) of white platelets, m.p. 155–156°. Analysis showed this compound to be an isomer of the foregoing furan II.

Anal. Calcd. for $C_{24}H_{18}O$: C, 89.41; H, 5.63. Found: C, 89.30; H, 5.55.

Whether the compound was 2,2-diphenyl-1,2-dihydronaphtho[2,1-b]furan (VI) or a *cis* or *trans* isomer of II was not conclusively determined. An attempted dehydrogenation with NBS by the procedure used with II showed that the 155–156° compound reacted more slowly with NBS than did II and scarcely any hydrogen bromide was evolved. However, the small amount of product obtained could not be sufficiently purified for identification.

No other compounds were isolated from the oxide–naphthol reaction. An 86.2% recovery of excess 2-naphthol was achieved.

Reaction of 1,1-Diphenylethylene Oxide with 2-Naphthoxide Ion.—To a stirred solution of 2-naphthol (4.3 g., 0.03 mole), sodium hydroxide (0.4 g., 0.01 mole) and water (4 cc.) at the temperature of a boiling water-bath was added 1,1-diphenylethylene oxide (2.0 g., 0.01 mole). This reaction was conducted under nitrogen with stirring and heating for 10 hours. The mixture was then taken up in carbon tetrachloride (300 cc.) and extracted with 4% sodium hydroxide (300 cc.). After the carbon tetrachloride layer was washed and dried over anhydrous sodium sulfate, removal of the solvent gave an oil from which, by fractional crystallization from heptane, was obtained 0.2 g. (6.0%), m.p. 200–202°, of 2-(2-hydroxy-1-naphthyl)-2,2-diphenylethanol (V). Identification was by means of a mixed melting point with the authentic compound.[5] No other pure compound could be obtained from this fraction.

Acidification of the alkaline layer with dilute hydrochloric acid and extraction with benzene gave, after benzene removal, a yellow oil. This was refluxed in benzene containing a small amount of *p*-toluenesulfonic acid monohydrate for 2 hours. The solution was then washed with dilute sodium hydroxide and the benzene removed under reduced pressure to give, after recrystallization from ethanol, 0.3 g. (9.4%), m.p. 170–172°, of the cyclized product, 1,1-diphenyl-1,2-dihydronaphtho[2,1-b]furan,[5] identified by a mixed melting point.

These results indicate that the reaction mixture contained at least a 15% yield of the phenol-alcohol resulting from nuclear attack on the 2-naphthol. No other compounds were isolated from the alkali-soluble fraction.

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