mg of allylic alcohol **6a** and the chromium trioxide (30 mg)–pyridine (2 ml) reagent (room temperature, 18 hr). The yield of ketone **5** melting at 211–213° was 22 mg. The yield (20 mg) was somewhat less employing 2% chromium trioxide in acetic acid (room temperature, 4 hr).

Bufotalin Acetate (1c). Method A. From Iodohydrin 7a. A solution of *N*-iodosuccinimide (25 mg) in acetone (0.5 ml)–water (0.5 ml) was added to an acetone (4 ml) solution of 3β-acetoxy-14-dehydrobufotalin (**6b**, 25 mg). The mixture was stirred for 30 min and allowed to remain at room temperature for 20 hr. The mixture was then diluted with sodium sulfite (25 mg in 1 ml of water), poured into ice–water, and extracted with chloroform. The combined extract was washed with water and concentrated to dryness to yield 24 mg of iodohydrin **7a**. A solution of the crude iodohydrin in methylene chloride was allowed to react with excess Urushibara nickel A with stirring (nitrogen atmosphere) at room temperature for 4 hr. The solution was filtered, solvent was evaporated, and the residue was chromatographed. Elution with 9:1 hexane–acetone led to 19 mg of bufotalin acetate as prisms melting at 263–269°.

Method B. From Bromohydrin 7b. The procedure of method A was repeated employing 20 mg of olefin **6b** and 20 mg of *N*-bromosuccinimide. In this experiment the reaction time was 19 hr and 12 mg of bufotalin acetate (**1c**, mp 265–269°) was realized. The overall yield of bufotalin acetate was essentially unchanged using *N*-bromoacetamide in place of *N*-bromosuccinimide.

Method D. From 3β,14β,16β-Trihydroxy-5β-bufa-20,22-dienolide (1d). A 20-mg sample of triol **1b** obtained *via* the ketone **4** route (**4** → **1b** → **1c** → **1d**) was acetylated with acidic anhydride (0.28 ml)–pyridine (0.4 ml) at room temperature over 18 hr. The crude acetone (22 mg) was recrystallized from acetone–hexane to yield 17 mg of bufotalin acetate (**1c**) melting at 263–269°. The specimens of bufotalin acetate prepared by methods A–C were found mutually identical.

Acknowledgments. We are pleased to acknowledge support of this investigation by the National Cancer Institute (performed pursuant to Contract No. N01-CM-12308 with the Division of Cancer Treatment, National Cancer Institute, Department of Health, Education and Welfare), the J. W. Kieckhefer Foundation, The Fannie E. Rippel Foundation, Mrs. Virginia L. Bayless, The Salt River Project of Arizona, The Arizona Public Service Co., and The Motorola Co.

Registry No.—**1a**, 471-95-4; **1b**, 4026-98-6; **1c**, 4029-69-0; **1d**, 465-19-0; **2**, 470-37-1; **3**, 36615-16-4; **4**, 35602-94-9; **5**, 51869-38-6; **6a**, 51869-39-7; **6b**, 36615-06-2; **7a**, 51869-40-0; **7b**, 51869-41-1; 3β-acetoxy-16β-hydroxy-14β,15β-epoxy-5β-bufa-20,22-dienolide, 4026-96-4.

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Deoxygenation of 1,4-Epoxy-1,4-dihydronaphthalenes, a Possible Cheletropic Removal of Oxygen[1]

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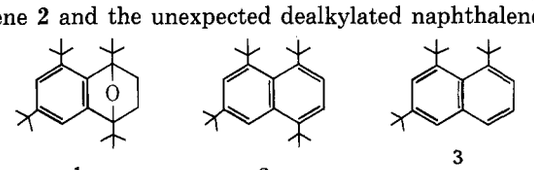
The one-step aromatization of benzyne–furan Diels–Alder adducts has been carried out in two ways. An apparent photochemical extrusion of atomic oxygen in triethylamine afforded a low yield of naphthalene. The use of naphthalene anion radical with substituted adducts proved to be a useful synthetic procedure.

In earlier work in our laboratory,[2] the acid-catalyzed dehydration of endoxide **1** afforded both the desired naphthalene **2** and the unexpected dealkylated naphthalene **3**.



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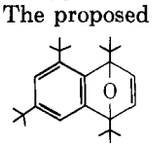
In addition, other dealkylations were observed, but the subject case was the most sensitive one. At the time, new routes to sensistive naphthalenes which would avoid acidic conditions were sought in our laboratory. One approach would be the direct deoxygenation of a benzyne–furan Diels–Alder adduct **4**. The proposed direct deoxygenation



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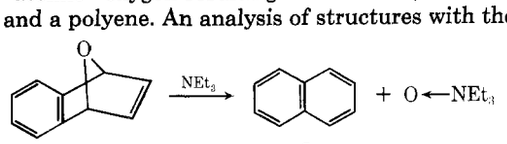
of endoxides such as **4** to form naphthalene **2**, is formally an *extrusion reaction*, examples of which are well known.[3] An approximate order of ease of extrusion is $N_2 > CO_2 > CO \geq$ "SO" $> SO_2 > O_2 \geq S > O$. Woodward and Hoffmann[4] describe a reaction and selection rules in which a tertiary amine reacts with a cyclic allyl ether so as to remove "atomic" oxygen resulting in the formation of an *N*-oxide and a polyene. An analysis of structures with the use



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of models shows that the bridgehead protons of **5** obstruct the "linear" approach of the tertiary amine (one of the alkyl groups of the amine) so that oxygen abstraction cannot occur. Thus, a "nonlinear" disrotatory reaction requiring photochemical activation is predicted as necessary for our desired synthesis.[5]

The photolysis of 1,4-dihydronaphthalene-1,4-endoxide

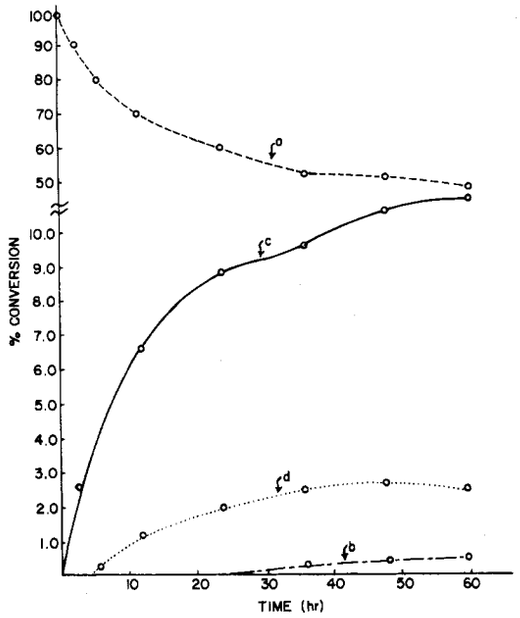
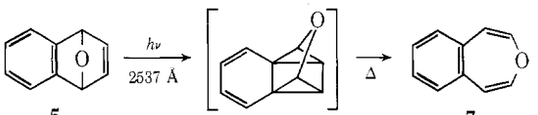


Figure 1. Irradiation of endoxide **5** at 2537 Å in ethanol: (a) endoxide **5**, (b) naphthalene (6), (c) benzoxepine **7**, (d) dihydroendoxide **9**.

(5) has been reported by Hammond and Ziegler.[6] They report that irradiation of an ethanol or ether solution of endoxide **5** afforded a 4–6% yield of the yellow benz[*l*]oxepine (**7**). The proposed intermediacy of a 7-oxaquadricyclane (**8**), which thermally rearranged to form **7**, was the first example of a $[_{\pi}2_3 + _{\pi}6_s]$ intramolecular cycloaddition.



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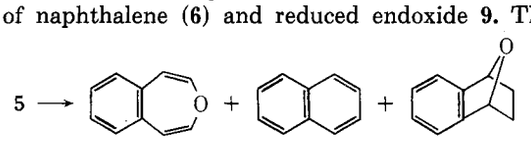
For this work, a reinvestigation of this reaction, monitored by glpc, revealed the formation of benzoxepine (**7**) and two other products, **9** and **6**. These products were found in 1–4% ether or ethanol solutions of starting endoxide **5** after irradiations for a significant period of time. What is most interesting is the observation of the formation of naphthalene (**6**) and reduced endoxide **9**. These



7 6 9

products were previously undetected, since they do not absorb radiation at 445 nm, at which wavelength the concentrations of benzoxepine **7** were determined by Ziegler and Hammond (Figure 1). Irradiation of the endoxide **5** as a solution in triethylamine at 253.7 nm produced a photolysate with the same products but different proportions. (Figure 2). The starting material is consumed at a much slower rate, so that at the same period of irradiation (60 hr) less than half of starting endoxide **5** is consumed in the amine solution as compared with the ethanol solution. The yield of benzoxepine **7** has been halved while the yield of naphthalene (**6**) has been increased 14-fold. The yield of reduced endoxide **9** has been multiplied by approximately 2.5. In going from ethanol to triethylamine, the total conversion of endoxide has diminished from 13.9 to 4.4%, yet the total yield of products, **6**, **7**, and **9**, has not changed significantly (27.5 to 26.0%).

Investigations into the nature of the excited state in tri-

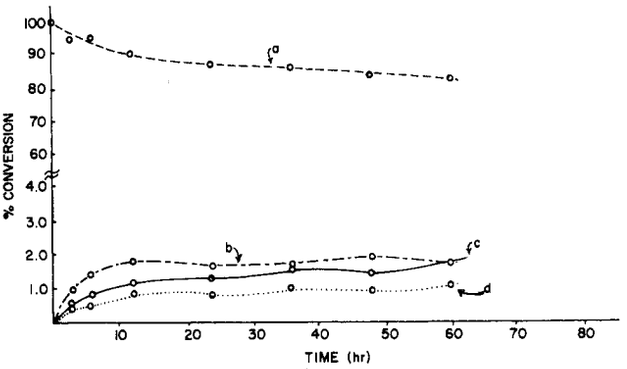


Figure 2. Irradiation of endoxide **5** at 2537 Å in triethylamine: (a) endoxide **5**, (b) naphthalene (**6**), (c) benzoxepine **7**, (d) dihydroendoxide **9**.

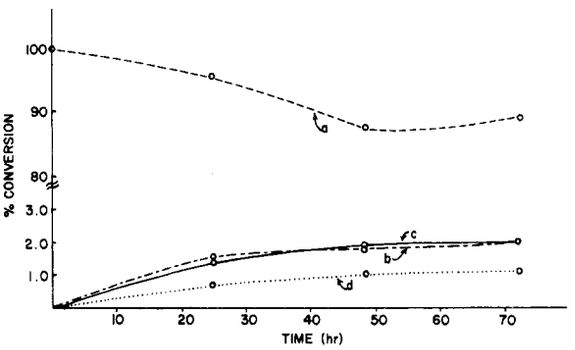


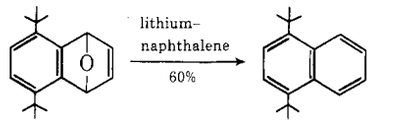
Figure 3. Irradiation of endoxide **5** at 2537 Å in triethylamine with added naphthalene: (a) endoxide **5**, (b) naphthalene formed in photolysis, (c) benzoxepine **7**, (d) dihydroendoxide **9**.

ethylamine were limited to the use of the lower energy triplet sensitizer, triphenylene (E_T = 67.2 kcal/mol; acetophenone, E_T = 76.3 kcal/mol). This was done to avoid the known reaction of aromatic ketones with tertiary amines in solution.[7] The photolysis of endoxide **5** in triethylamine in the presence of triphenylene produced only gummy, intractable material and no formation of **7**, **9**, or **6** was detected. Therefore, we assume that naphthalene (**6**) in addition to benzoxepine **7** and reduced endoxide **9** came from the singlet state of endoxide **5**. As the concentration of naphthalene (**6**) increases in triethylamine solution during the course of the reaction, it should compete with the other products and starting material for absorption of the available ultraviolet light. If this is true and the aromatic products do not react further, the overall disappearance of starting endoxide **5** should proceed more slowly. A solution of endoxide **5** in triethylamine was irradiated in the presence of the quantity of naphthalene which would have been the final amount produced. Figure 3 describes the progress of the reaction. At 60 hr, only 12% of the endoxide was consumed compared to 18% in the absence of naphthalene (Figure 3). Actual product distribution was not changed greatly in the presence of this aromatic hydrocarbon.

Several questions may arise pertaining to the actual source of naphthalene (**6**) in these photolyses. When the reduced endoxide **9** is treated with acid,[8] an excellent yield of naphthalene is obtained. If this dehydration could occur in the photolysate of endoxide **5**, this process might be the main source of naphthalene (**6**). An authentic sample of reduced endoxide **9** was irradiated in triethylamine under the same conditions as irradiation of endoxide **5**. After 48 hr, only 1.8% yield of naphthalene was detected while 71% of the starting reduced endoxide **9** was consumed. Compound **9** is, therefore, only a very minor source of naphthalene.

Since the yield of benzoxepine **7** was decreased in triethylamine while that of naphthalene (**6**) was increased, it might be argued that benzoxepine was the source of naphthalene.[9] Benzoxepine **7** was irradiated with a low-pressure mercury lamp under conditions comparable to the triethylamine–endoxide **5** photolysis. No naphthalene was detected even after irradiation for 107 hr. As a result, benzoxepine **7** is not considered to be a source of naphthalene (**6**). In addition, the products, **7, 9,** and **6,** of photolysis are not the result of a thermal reaction of endoxide **5.** A solution of endoxide **5** in the amine was warmed at 90° for 77 hr and no trace of **7, 9,** or **6** could be detected. Thus, our photochemical experiments demonstrate a deoxygenation process. We cannot specify the actual intermediate that is being deoxygenated. It could be the singlet excited state of **5,** quadricyclic **8,** or some electron-rich species which would account for both deoxygenation to form naphthalene and hydrogen abstraction to form reduction product **9.**

Our experiments focused on the use of anion radicals for the following reasons. Double bonds, both isolated and conjugated, can be photoreduced.[10] Furthermore, many mechanistic explanations for this reduction include charge transfer, exciplex formation, and/or radical anion intermediacy.[11] It was therefore conceivable that our photochemistry was simply serving as a fairly inefficient technique for forming the radical anion of **5,** only one of the several possibilities for deactivation of the excited singlet of **5.** Therefore, the production of the radical anion, which would bypass the undesirable photochemical products, was investigated.[12] We used lithium naphthalenide as our electron source and endoxides **4** and **11** as substrates. In clean conversions, the desired substituted naphthalenes were produced.



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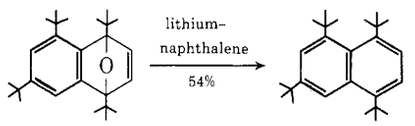

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Experimental Section

General. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer Models 137 and 337 spectrometers. Ultraviolet spectra were determined on a Cary 15 spectrophotometer. Proton magnetic resonance spectra were recorded on a Varian A-60A instrument at probe (38°) temperature. Signals are reported downfield from tetramethylsilane. An F & M 810 gas chromatograph with flame ionization detectors and a Honeywell 16 recorder with a disk integrator was used for qualitative and quantitative determinations. The carrier gas was nitrogen at a flow rate 30–40 ml/min. The columns used in this work were A, 6 ft × 0.125 in., 10% silicone gum rubber SE-30 on 80–100 mesh Chromosorb WAW-DMCS; B, 6 ft × 0.25 in., 10% polyphenyl ether (six ring) on 60–80 mesh Chromosorb WAW-DMCS; C, 5 ft × 0.125 in., 15% XF-1150 on 60–80 mesh Chromosorb W; D, 8 ft × 0.125 in., 15% XF-1150 on 60–80 mesh Chromosorb W; E, 8 ft × 0.125 in., 5% Carbowax 20M on 80–100 mesh Chromosorb WAW; F, 8 ft × 0.125 in., 10% XE-60 on 50–100 mesh Anakrom ABS; G, 5 ft × 0.125 in., 10% QF-1 on 60–80 mesh Chromosorb W.

Calibration curves were determined by measuring the glpc response of a known with respect to that of a known quantity of 1-menthol and subjecting these ratios to a least-squares analysis for fitting a straight line to a series of points.[13] Errors in yields and conversions are within a 10% relative standard deviation. The calibration curves for 1,4-dihydronaphthalene-1,4-endoxide (**5**), naphthalene (**6**), and 1,2,3,4-tetrahydronaphthalene-1,4-endoxide (**9**) were prepared by this method. Benzoxepine (**7**) could not be isolated in pure enough state to prepare such a curve. Calibration curves were checked every few months for the correlation, within experimental error, of known *vs.* calculated data.

Photolysis of 1,4-Dihydronaphthalene-1,4-endoxide (5). A. Triethylamine. (1) A 1% solution of endoxide **5** in distilled triethylamine[14,15] was irradiated[16] for 194 hr in a water-jacketed quartz-well photolysis apparatus under a nitrogen atmosphere and magnetically stirred. The resulting amber, cloudy solution was evaporated to give an amber oil. A vpc on column B (200°) indicated the major constituent to be the starting endoxide with minor amounts of materials with retention times of benzoxepine and naphthalene. The dark green solid which adhered to the immersion well was scraped off and this amounted to 5% by weight of starting material. It was insoluble in benzene, hexane, acetone, ethyl ether, and water but soluble in methylene chloride and chloroform. Its melting point was above 350° and it had weak and broad absorptions in the infrared spectrum (KBr) at 2890, 1620, 1580, 1440, 800, 752, and 685 cm^{-1}.

The amber oil above was chromatographed on a column of silica gel and eluted with a gradient of hexane to ether. The fractions were each analyzed by glpc (column B) and combined on this basis. The later fractions (25–40% v/v ether in hexane) contained mainly starting endoxide. This was sublimed and recrystallized from pentane.[17] Thirty-six per cent of the starting endoxide (**5**) could be recovered.

The earlier fractions (20–25% v/v ether in hexane) contained mixtures of naphthalene (**6**), benzoxepine **7,** and endoxide **5.** These were combined and submitted to preparative gas–liquid partition chromatography. Naphthalene (**6**) was isolated in a yield of 0.80% and was confirmed by its infrared spectrum and by peak enhancement techniques in glpc. After two sublimations (low vacuum), the melting point was 78–81° (lit. mp 80.2°).

The yellow benzoxepine **7** was also isolated by this preparative glpc and sublimed in 0.67% yield: mp 82–83° (lit. mp 83–84°);[18] ir (CCl_4) 1658 and 1631 (enol ether), 1486, 1431, 1049 cm^{-1}.

(2) A quartz nmr tube was filled with a 2–6.5% solution of endoxide **5** (*ca.* 100–200 mg) in distilled triethylamine (*ca.* 2.5 ml) and was stoppered with a serum cap. This solution also contained menthol as a standard in amounts equal to 10% of the weight of endoxide. The air above the solution was exchanged for nitrogen or argon *via* a hypodermic syringe. The tube was inverted several times to ensure homogeneity. It was suspended 3 cm from a low-pressure Hg lamp and irradiated.

Samples were withdrawn with a hypodermic syringe through the septum at various time intervals. Each sample was analyzed several times by glpc on column C or D at 100–120°. A significant number of analyses were taken so that the relative standard deviation of R (the ratio of $area_i$ to $area_{standard}$) was less than 10% (usually less than 5%).

(3) A 5.1% solution of endoxide **5** in distilled triethylamine (0.71 mmol in 2.0 ml) containing 0.0094 g of menthol was placed in a quartz nmr tube. This solution contained 0.041 mmol of naphthalene (**6**), an amount which reflected the final per cent conversion (*ca.* 6%) expected in its absence. The analytical procedure was as stated above.

(4) Repeating the procedure with the quartz nmr tube described above, a 6.5% solution of 0.1629 g (1.13 mmol) of endoxide **5** and 0.0161 g of menthol was irradiated by a low-pressure Hg lamp for 60 hr. Analysis of the reaction mixture was made by glpc (column D, 150°) and the amount of naphthalene (**6**) was carefully determined. Infrared spectra were taken of the reaction mixture at time zero and 60 hr. A sample of triethylamine *N*-oxide (3.45 mg) was added to the irradiated reaction mixture. Infrared spectra were taken of this new reaction mixture and the spectra before and after addition were compared.

B. In Ether or Ethanol. (1) A solution of 1.122 g (7.8 mmol) of endoxide **5** in 110 ml of anhydrous ethyl ether was irradiated for 48 hr under nitrogen with a low-pressure Hg lamp in a quartz photolysis vessel.

Evaporation of the yellow solution gave 1.193 g of an amber syrup. The glpc on column B verified the presence of starting endoxide **5,** naphthalene (**6**), and benzoxepine **7.** This oil was chromatographed on a column of 60 g of activated silica gel and eluted with a gradient of hexane to 5% ether in hexane (v/v). The fractions were each analyzed by glpc. Those which contained benzoxepine also contained naphthalene and endoxide. They were com-

bined to give 0.238 g of a yellow solid, mp 50–65°). Recrystallization from MeOH–H_2O gave 0.112 g of a yellow solid, mp 80–83° (lit. mp 83–84°[18]). The mother liquor was extracted with ether and dried over sodium sulfate. This was subjected to two 1-g columns of silica gel to increase the isolated yield to 11.1%: ir (CCl_4) 1664 and 1631 (enol ether), 1486, 1431, 1311, 1049 cm^{-1}.

In another attempt to obtain pure benzoxepine, the crude reaction mixture was chromatographed by dry column technique on alumina (CCl_4 eluent). The yellow band was extracted and rechromatographed on silica gel by dry-column technique using pentane as eluent. This gave a 6.4% yield of a yellow solid which was only approximately half benzoxepine by glpc analysis (column C, 165°).

(2) A 4% solution of 0.1056 g (0.733 mmol) of endoxide **5** and 0.0175 g of menthol in 2.5 ml of absolute ethanol was used to fill a quartz nmr tube. The tube was stoppered with a serum cap and the air above the solution was exchanged for argon *via* a syringe. The tube was inverted several times to ensure the homogeneity of the solution and irradiated at a distance of 3 cm from a low-pressure Hg lamp. Samples were removed at various time intervals and subjected to glpc analysis on column C at 110°.

C. In the Presence of a Sensitizer. In a quartz nmr tube described above, a 4.4% solution of endoxide **5** in distilled triethylamine was irradiated in the presence of triphenylene (0.15%) with a 450-W Hanovia medium-pressure mercury-arc lamp with a Kimex filter. After 48 hr, the solution was filtered and the residue was washed with benzene. Washings were added to the filtrate, which was then concentrated and a known amount of standard added.

Deoxygenation with Radical Anion Naphthalene. The stock solution of lithium radical anion naphthalene was prepared in both dry THF and 1,2-dimethoxyethane.[19] Small strips of lithium wire (0.0104 mol) were added to a solution of 0.0111 mol of naphthalene in 30 ml of dry solvent under an argon atmosphere. The blue-green color of the radical anion appeared within 2 hr. The solution was stirred (glass-covered stirring bar) overnight. This mixture was used in the deoxygenations of two endoxides.

A. 1,4,5,7-Tetra-*tert*-butyl-1,4-dihydronaphthalene-1,4-endoxide (4). A 4.20-mg portion of this endoxide (4) was stirred in 1 ml of dry DME under an argon atmosphere. One milliliter of the stock radical anion solution was injected dropwise from a syringe over 10 min. Coloration persisted for 2 hr at ambient temperatures. The dark green mixture was decomposed with an iodine crystal and the resulting colorless, cloudy suspension was evaporated *in vacuo*. The residue was suspended in 10 ml of ether and then washed with 5 ml of 1 *N* sodium thiosulfate solution. The organic layer was then washed with 5 ml of water and 5 ml of saturated sodium chloride solution and dried over sodium sulfate.

Evaporation gave 83 mg of a semisolid which was sublimed at 45° (10 mm) for 1.5 hr to remove naphthalene. The amber residue (7 mg) was chromatographed by thin layer chromatography on magnesium silicate (20 × 20 cm plate, 0.1-mm thickness, eluent pentane). The major spot (R_f 0.90–0.74) was extracted with benzene and methylene chloride to give 3 mg of an oily solid. This was rechromatographed on a quarter plate of magnesium silicate to give 2.15 mg (53.5% yield) of a semisolid which was pure by glpc (column A, 230°) and which proved to be 1,4,5,7-tetra-*tert*-butylna phthalene (2) by peak enhancement and comparison of the infrared spectrum with that of authentic samples.

B. 5,8-Di-*tert*-butyl-1,4-dihydronaphthalene-1,4-endoxide (11).[20] A 10.5-mg portion of this endoxide (11) was stirred (glass-covered stirring bar) in 2 ml of dry DME under an atmosphere of argon. The radical anion solution in DME was injected slowly until the blue-green color did not discharge (*ca.* 2 ml). The mixture was allowed to stir for 1 hr at room temperature. A sample was removed, decomposed with water, and extracted with ether. The organic layer was concentrated and subjected to glpc analysis (column C, 175°). The presence of naphthalene and 1,4-di-*tert*-butylnaphthalene (12) was confirmed by peak enhancement. No starting endoxide was evident.

The reaction mixture was decomposed with an iodine crystal and evaporated. The residue was taken up in ether, washed with 5 ml of 1 *N* sodium thiosulfate solution, water, and saturated brine, and dried over magnesium sulfate. Evaporation of solvent gave 20 mg of semisolid.

This was sublimed at room temperature at 14 mm to remove naphthalene. The yellowish residue (12 mg) was chromatographed by thin layer technique on magnesium silicate (20 × 20 cm plate, 0.1-mm thickness, eluent CCl_4). the major spot (R_f 0.75–0.60) was extracted with methylene chloride. Evaporation of solvent gave 6 mg (61% yield) of a semisolid which was 1,4-di-*tert*-butylnaphthalene (12) by peak enhancement of glpc and by comparison of ir of authentic samples. A similar procedure in THF gave only 50% yield.

Registry No.—**4**, 22495-83-6; **5**, 573-57-9; **11**, 10565-41-0.

References and Notes

(1) (a) Portions of this work have been presented at the Autumn Meeting of the Chemical Society, London, Oct 1970, Abstracts, A 10. (b) Taken from the Ph.D. Thesis of S. B. P., Fordham University, 1973. (c) Acknowledgment for partial financial support is made to the National Science Foundation (Grant GP 7754), the National Institutes of Health (CA 11421), and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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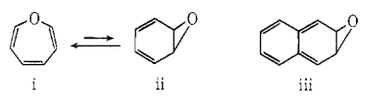

i ii iii

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(15) Dried over potassium hydroxide and distilled from a 2% solution of naphthyl or phenyl isocyanate (triethylamine bp 89°).

(16) Low-pressure mercury-arc lamp whose output is greater than 90% at 2537 Å.

(17) A solid which was insoluble in pentane; proved to be α-naphthol by infrared spectrum and glpc retention time.

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