

An attempt to generate tetrachlorocyclobutadiene from hexachlorocyclobutene and diiron nonacarbonyl gave no products readily elutable from alumina. Reaction of hexachlorocyclobutene with disodium iron tetracarbonyl resulted in a low yield of tetrachlorocyclobutadiene dimer, indicative of the intermediacy of tetrachlorocyclobutadiene, but no indication of a stable chlorocarbon complex with iron was found.

Experimental Section

Preparation of Dichloroacetylene. Solutions of dichloroacetylene in ether were prepared by a literature procedure.² As claimed by these authors, the liquid phase synthesis seems to greatly reduce the danger of explosion during preparation, so that C_2Cl_2 -ether solutions were prepared and allowed to react without incident in the present work. In view of the explosion and toxicity hazards, however, dichloroacetylene should be confined to the hood and proper shielding and protective clothing should be used.

A typical synthesis was carried out with a solution of 1000 g of 85% KOH pellets in 700 ml of glycol heated at 140° and stirred with a paddle stirrer. The system was kept under an inert atmosphere by a slow stream of nitrogen (100 cm³/min) while a mixture of 656 g (5.0 mol) of trichloroethylene and 370 g (5.0 mol) of ether was added at a rate of 3–5 ml/min over a period of 4–5 hr. Product was collected as formed in a receiver cooled at –80° and topped by a –15° condenser. When the addition was completed and the system purged with nitrogen, the liquid product was decanted from the ice, dried at 25°, and distilled through a Widmer column. The fraction with bp 33–35° was taken after a small foreshot containing volatile impurities was discarded. The C_2Cl_2 -ether cut, 344 g, was assayed by gc with a column of 30% didecyl phthalate on 60–80 mesh Chromosorb W held at 50°. Ether has the shorter retention time on this column.

Using 0.67 as the gc weight factor for ether, three determinations gave 0.87, 0.73, and 0.80 for an average value of 0.80 as the weight factor for dichloroacetylene. With these weight factors, the concentration of C_2Cl_2 in the above preparation was found to be 19%. The conversion was 14% and the yield based on 276 g of unrecovered trichloroethylene was 33% (65.4 g) of C_2Cl_2 .

Tetrachlorocyclopentadienoneiron Tricarbonyl (1). A mixture of 9.5 g (0.10 mol) of C_2Cl_2 in ~50 ml of ether and 9.1 g (0.025 mol) of diiron nonacarbonyl was stirred at 25° for 1 day, by which time the initial moderate gas evolution had ceased. Gc indicated the C_2Cl_2 to be more than half gone. Another 9.1 g (0.025 mol) of $Fe_2(CO)_9$ was added and the mixture was stirred another day. Only a trace of C_2Cl_2 remained. The dark mixture was filtered and the solid extracted several times with ether. Evaporation of the combined ether solutions to 50° (0.5 mm) gave a mixture of crystals and amorphous solid as residue. This residue was dissolved in dry benzene, filtered, and chromatographed on an 8.5 in. × 1.5 in. column of Woelm neutral alumina. Elution with 1:1 benzene-pentane rapidly removed 0.68 g (7%) of hexachlorobenzene, mp 223.5–225.5° after recrystallization from benzene, identified by comparison of its ir spectrum with that of a known sample.

Elution with tetrahydrofuran gave 1.5 g of yellow-orange crystals, mp 101–102°. Further elution with 3:1 tetrahydrofuran-methanol gave another 3.3 g of crystals, mp 100–102°, followed closely by a mixture of crystals and amorphous dark material. The combined crops of product, 4.8 g, are 27% tetrachlorocyclopentadienoneiron tricarbonyl. An analytical sample was recrystallized from pentane: mp 101–102°; ir (KBr) 4.73 and 4.85 (Fe–CO), 5.78 (sh) and 5.94 (conjugated C=O), 7.27, μ (coordinated CCl=CCl).

Anal. Calcd for $C_8Cl_4FeO_4$: C, 26.86; Cl, 39.64; Fe, 15.61; mol wt, 357.7. Found: C, 26.94; Cl, 39.39; Fe, 15.70; mol wt, 351 (vp osmometry, PhH at 37°).

Diels-Alder Addition to Dichloroacetylene. At 25–65°, C_2Cl_2 undergoes Diels-Alder addition to only the most reactive dienes. Thus, no reaction was detected with tetraphenylcyclohexene at 65°, and a very slow oxygen-initiated polymerization to C_2Cl_2 -diene- O_2 terpolymer occurred with 2,3-dimethylbutadiene at 35°. However, 1,3-diphenylisobenzofuran reacted readily with C_2Cl_2 at 65°.

A solution of 1.35 g (0.005 mol) of 1,3-diphenylisobenzofuran and 1.9 g (0.02 mol) of C_2Cl_2 in ~15 ml of ether and 50 ml of dry benzene was refluxed (65°) for 3 days, during which time the color lightened after 3–4 hr, and then darkened. Solvents were removed, the residue was extracted with hexane, and the hexane solution was concentrated to give 0.45 g of nearly colorless crystals, mp 134–135°. A second crop, 0.71 g, mp 132–134°, raised the total of 1.16 g (64%)

of 2,3-dichloro-1,4-diphenyl-1,4-epoxynaphthalene (2). A sample was recrystallized from hexane for analysis: mp 134.5–135°; ir (KBr) 3.26 (=CH), 6.22 and 6.67 (aromatic C=C), 9.0 and 9.9 (may be COC), 13 and 14 μ (mono- and disubstituted aromatic).

Anal. Calcd for $C_{22}H_{14}Cl_2O$: C, 72.34; H, 3.86; Cl, 19.41. Found: C, 72.69; H, 4.17; Cl, 19.43.

Cyclopentadiene did not react with C_2Cl_2 in 1 day at 25°, but Diels-Alder addition was observed at 100° for 15 hr. Distillation of the 100° reaction mixture gave, in addition to tars, a low yield of 2,3-dichlorobicycloheptadiene³ codistilling at ca. 68° (22 mm) with dicyclopentadiene. The components of the mixture were identified by ir, nmr, and gc-mass spectrometry.

Tetrachlorocyclobutadiene Dimer.⁴ A number of highly chlorinated olefins were exposed to diiron nonacarbonyl and to disodium iron tetracarbonyl. In some cases, little interaction occurred at 25–50°. In others, any iron-chlorocarbon complexes which may have been formed were readily decomposed.

Reaction of $Fe_2(CO)_9$ with hexachlorocyclopentadiene occurred readily at 25° to give 19% of decachlorodicyclopentadienyl as the only product isolated by chromatography. A related compound with no allylic chlorine, 5,5-dimethoxytetrachlorocyclopentadiene, did not react readily with $Fe_2(CO)_9$ at 50°. Similarly, the diene system in tetrachloro- α -pyrone did not appear to react with $Fe_2(CO)_9$ at 25–50°, and hexachlorocyclobutene reacted poorly.

A more nucleophilic reagent, disodium iron tetracarbonyl, reacted with hexachlorocyclopentadiene at 0–25° with formation of a black, amorphous insoluble solid. With hexachlorocyclobutene, disodium iron tetracarbonyl reacted exothermically to give (after chromatography and recrystallization) 5% of tetrachlorocyclobutadiene dimer, mp 160.5–161.5°, after recrystallization from methylene chloride-hexane.

Anal. Calcd for C_8Cl_8 : C, 25.31; Cl, 74.69. Found: C, 25.72; Cl, 74.24.

The ir spectrum corresponded to that reported in the literature,⁴ as did the melting point.

Registry No.—1, 53336-51-9; 2, 53336-59-7; dichloroacetylene, 7572-29-4; diiron nonacarbonyl, 20982-74-5; 1,3-diphenylisobenzofuran, 5471-63-6; hexachlorocyclopentadiene, 77-47-4; disodium iron tetracarbonyl, 14878-31-0; tetrachlorobutadiene dimer, 53336-52-0.

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Synthesis of 1,4-Dihydro-1,4-dimethyl-1,4-epoxynaphthalene and Conversion to 1,4-Dimethyl-1,2,3,4-tetrahydronaphthalene and *o*-Diacylbenzene¹

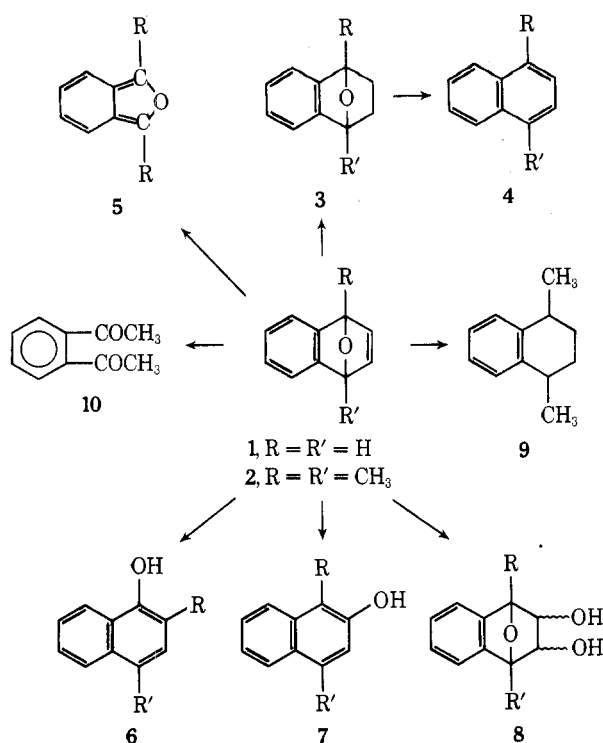
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Received August 29, 1974

Compounds of the type 1,4-dihydro-1,4-epoxynaphthalene (1) are of synthetic interest because they can be synthesized from the reaction of a benzyne with a furan⁴ and transformed into a variety of naphthalene derivatives in good yields by relatively simple experimental procedures. For example, the parent 1 (R = R' = H) was reduced to the tetrahydro derivative 3 (R = R' = H), which on treatment with methanolic acid yielded naphthalene 4 (R = R' = H) in 90% yield.⁵ Obviously, a variety of 1-monosubstituted and 1,4-disubstituted naphthalenes are accessible by this route. By more involved chemistry, the availability of the

Scheme I



unstable dialkylisobenzofurans (5), which may be trapped *in situ*, are accessible.⁶ Acid-catalyzed rearrangements of 2 have been shown to yield both 2,4-dimethyl-1-naphthol (6) and 1,4-dimethyl-2-naphthol (7) depending on reaction conditions,^{7,8} whereas oxidation yields the glycols,⁸ 8. In the work herein described we report an improved synthesis of 1,4-dihydro-1,4-dimethyl-1,4-epoxynaphthalene (2) from *o*-bromofluorobenzene (via benzyne) and 2,5-dimethylfuran,⁴ as well as the one-step conversions of 2 to 1,4-dimethyl-1,2,3,4-tetrahydronaphthalene (9) and *o*-diacetylbenzene (10). The versatility of 2 as an intermediate is increased by realizing that it, and analogous compounds, can also be made by the generation of benzyne from anthranilic acid derived precursors.⁴ The transformations discussed above are outlined in Scheme I.

Many syntheses of 9, which involved double alkylation of benzene with dichlorohexanes⁹ or diallyl,¹⁰ have been reported but all suffer from low yields and/or the lack of proof of structure and purity of the product obtained. Cyclization of 5-phenyl-2-hexanol¹¹ and 5-phenyl-2-hexanone¹² to 9 by acid has also been reported. Perhaps the best previous method is that involving the catalytic reduction of 1,2-dihydro-1,4-dimethylnaphthalene¹³ prepared previously by a multistep synthesis from benzene and succinic anhydride.¹⁴ We have found that catalytic reduction of 2 affords 9 rapidly in almost quantitative yield. This finding stands in contrast to the earlier report⁵ that hydrogenation of 1 (R = R' = H) over Pd/C yielded 3 (R = R' = H) which did not further absorb hydrogen. However, no details as to catalyst or hydrogen pressure were given.⁵ We assume that 9 is the *cis* isomer because catalytic reduction of benzylic alcohols and epoxides has been shown to proceed with inversion.¹⁵

o-Diacetylbenzene (10) has been prepared by many methods¹⁶ but all suffer from low yields, rare starting materials, or both. We have found that oxidation of 2 using the Starks phase transfer method¹⁷ yields 10 in 69% yield. Undoubtedly, this route could be used to synthesize other *o*-diacetylbenzenes.

The synthesis of the key intermediate 2 via *o*-bromofluorobenzene and 2,5-dimethylfuran⁴ and the synthesis of 2,5-dimethylfuran have been improved.

Experimental Section¹⁸

2,5-Dimethylfuran. A 50-ml Claisen flask containing 13.0 g of freshly fused zinc chloride was fitted with a dropping funnel containing 100 g of freshly distilled 2,5-hexanedione and a magnetic stirrer. About 10 ml of the dione was added and the flask was heated with a bath held in the 150–160° range. Distillation of a two-phase distillate soon took place. The reaction volume was kept about constant by addition of dione. The temperature of the distillate varied from 90 to 95°. All of the dione was added at such a rate that after 3 hr the entire product had been collected. The organic layer of the distillate was separated from the aqueous layer, dried over anhydrous MgSO₄, and distilled through a short column to yield 60 g (71%) of pure 2,5-dimethylfuran, bp 92.5–93.0°, which remained colorless at room temperature for several days.¹⁹ After this procedure had been worked out we repeated the procedure which uses Amberlyst 15 (a cationic resin).²⁰ In our hands the yield was good but the product invariably colored on standing even after distillation. Perhaps our batch of catalyst was different from that used previously.

1,4-Dihydro-1,4-dimethyl-1,4-epoxynaphthalene (2). In a 100-ml three-necked thoroughly dried flask equipped with a reflux condenser, mechanical stirrer, and pressure-equalizing dropping funnel were placed 0.8 g (0.033 g-atom) of sublimed magnesium,²¹ 2.8 g (0.03 mol) of 2,5-dimethylfuran, and 15 ml of tetrahydrofuran (THF). After flushing with dry nitrogen the mixture was heated to reflux and a solution of 5.26 g (0.03 mol) of freshly distilled *o*-bromofluorobenzene in 10 ml of THF was added dropwise during 15 min. After 2 hr at reflux the reaction mixture was cooled and treated with ammonium chloride solution. A conventional work-up afforded 4.66 g (90%) of 2: bp 131–134° (about 45 mm) (house vacuum); nmr (CDCl₃) τ 8.66 (s, 6, CH₃), 3.43 (s, 2, vinyl H), and 3.13 (symmetrical m, 4, ArH). Ref 6b gives 2, bp 120° (35 mm), and ref 7a gives mp 35°.

In earlier synthesis of 2 from 2,5-dimethylfuran and diazotized anthranilic acid, the furan was used in 100% excess.²² In view of the present lack of availability of this reagent, our present synthesis may be the most efficient with regard to 2,5-dimethylfuran.

1,4-Dimethyl-1,2,3,4-tetrahydronaphthalene (9). A mixture of 10.0 g of 2 and 0.5 g of 10% Pd/C²³ in 75 ml of pure methanol was shaken at 40 psi of hydrogen in a Parr apparatus. Absorption of hydrogen ceased after 20 min. After a conventional work-up 9.0 g (97%) of 9 [bp 63–64° (0.4 mm); nmr (CDCl₃) τ 8.80 (d, 6, CH₃), 8.39 (m, 4, CH₂), 7.32 (m, 2, CH), 3.03 (s, 4, ArH); mass spectrum *m/e* 160; 98% pure by glpc]²⁴ was obtained by distillation through a small column.

***o*-Diacetylbenzene (10).** A well-ground mixture of 63.2 g (0.4 mol) of KMnO₄ and 48 g (0.4 mol) of anhydrous MgSO₄ was added through a length of Gooch tubing to a well-stirred mixture of 17.2 g (0.1 mol) of 2, 0.5 g of Aliquat 336,²⁵ 450 ml of benzene, and 450 ml of water in a 2-l. three-necked flask at such a rate that gentle reflux occurred (30–60 min). After a further reflux for 30 min and a conventional work-up which included thorough washing of the MnO₂ with acetone there was obtained 11.2 g (69%) of 10, bp 95–98° (0.08 mm) (ref 16c reports a bp of 148–150° (14 mm)). The 2,4-DNPH derivative melted at 210° dec.²⁶

Registry No.—2, 4705-93-5; 9, 4175-54-6; 10, 704-00-7; 2,5-dimethylfuran, 625-86-5; 2,5-hexanedione, 110-13-4; *o*-bromofluorobenzene, 1072-85-1.

References and Notes

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- (18) All melting and boiling points are uncorrected. The nmr equipment used was purchased in part with funds granted to the Department of Chemistry by the National Science Foundation.
- (19) This preparation is modeled after that of F. Dietrich and C. Paal, *Chem. Ber.*, **20**, 1085 (1887); I. M. Heilbron, E. R. H. Jones, P. Smith, and B. C. L. Weedon, *J. Chem. Soc.*, **54** (1946).
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- (21) We have run this reaction only with sublimed magnesium. Hence we cannot say whether the improved yield is due to the magnesium or to the scrupulous care used in obtaining pure starting materials and solvent.
- (22) See L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963), for many references.
- (23) Obtained from Engelhardt.
- (24) A column, 8 ft \times 0.25 in., packed with 30% silicone gum rubber, SE-30, on fire brick in a Varian Aerograph A90-P3 apparatus, was used.
- (25) Methyltricaprylammonium chloride obtained from the General Mills Co., Kankakee, Ill.
- (26) S. Goldschmidt and A. Zoebelin, *Chem. Ber.*, **94**, 169 (1961), give a mp of 210°.

Selenium Dioxide Oxidation of *d*-Limonene. A Reinvestigation¹

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Received July 1, 1974

In several studies³⁻⁶ of the selenium dioxide oxidation of limonene (1), the tertiary alcohol 3 has been reported to be formed in yields varying from only a trace to almost 40%.³ Although some authors^{3,6,7} have worried about why the less electron-rich disubstituted double bond was preferentially attacked by selenium dioxide, it is not so surprising in view of the fact that oxymercuration⁸ and especially the ene reaction with formaldehyde⁹ both preferentially attack the disubstituted olefinic linkage in limonene (1).

The great enigma in connection with the *d*-limonene oxidation, however, was the reports^{3,6} that the product alcohol 3 was optically active. In the body of their paper Trachtenberg and Carver³ made no mention of the fact that 3 was optically active, but, in the Experimental Section they report for alcohol 3 $[\alpha]_D +13.6^\circ$ (neat, isolated by preparative glc). It should be noted that this formation of optically active alcohol 3 is inconsistent with their proposed mechanism.⁷ Wilson and Shaw⁶ reported $[\alpha]^{29D} -43.0^\circ$ (*c* 1.24, isolated by preparative glc) for alcohol 3 and noted that the formation of this optically active product was inconsistent with all of the proposed mechanisms for the selenium dioxide oxidation of olefins.^{10,11} Sakuda⁴ reported $[\alpha]_D +1.40^\circ$ for 3 but said that this small rotation could be ascribed to impurities in the product. Thomas and Bucher⁵ reported $[\alpha]_D 0^\circ$ for their distilled alcohol 3.

The mechanism which we have proposed¹¹ for the selenium dioxide oxidation of olefins (Scheme I) would involve an initial ene reaction between selenous acid and *d*-limonene followed by dehydration to produce the allylseleninic acid 2. A [2, 3] sigmatropic rearrangement followed by solvolysis would then give the product $\Delta^{1,8(9)}$ -*p*-menthadien-4-ol (3). According to this mechanistic sequence, the reac-

Scheme I

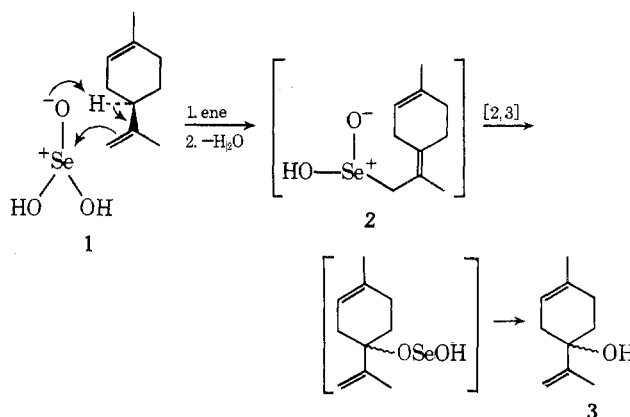


Table I
Experimental Conditions for the
 $\text{SeO}_2\text{-H}_2\text{O}_2$ Oxidation of *d*-Limonene

Expt	SeO_2 , mmol	H_2O_2 , mol	<i>d</i> -Limonene, mol	Reaction time
a	32	0.66	0.6	4 hr
b	32	0.66	0.3	4 hr
c	16	0.66	0.6	4 hr
d	32	0.66	0.6	20 min

tion proceeds through the symmetric allylseleninic acid 2; thus, the allylic alcohol 3 would be produced as the racemate. Therefore, Wilson's and Shaw's⁶ claim of optically active alcohol 3 was incompatible with our proposed mechanism.¹¹

We have repeated all of the four *d*-limonene oxidations reported by Wilson and Shaw.⁶ The reaction conditions are summarized in Table I and are described more fully in ref 6. The procedure of Thomas and Bucher⁵ was used to synthesize an authentic sample of alcohol 3. Glc of the above four reaction product mixtures indicated that each reaction did yield some of the alcohol 3, along with at least 27 other products. Experiment a was examined in order to determine the optical activity of the product alcohol 3, formed in 0.2% yield (by glc). Isolation of alcohol 3 by distillation followed by preparative glc resulted in a material which showed optical activity; $[\alpha]^{29D} +11.9^\circ$ (*c* 1.27). Although this material appeared to be homogeneous when examined by glc on OV-17, it showed several impurities on DEGS, which could possibly have been responsible for the observed rotation. The alcohol 3 was then isolated again, this time using a more elaborate purification sequence.

After a rapid distillation, the alcohol 3 was isolated by preparative tlc followed by preparative glc on an OV-17 column. This alcohol was then further purified by another preparative glc on a DEGS column. This very pure alcohol 3 was optically inactive; $[\alpha]^{29D} 0.000^\circ$ (*c* 1.27). That alcohol 3 had survived this sequence follows from the observations that the ir of the purified material was identical with that of authentic alcohol 3 and the melting point of the purified material's phenylurethane was not depressed by admixture of the phenylurethane of authentic alcohol 3.¹²

We submit, therefore, that the selenium dioxide oxidation of *d*-limonene (1) results in racemic $\Delta^{1,8(9)}$ -*p*-menthadien-4-ol (3), as predicted by our mechanism¹¹ and as shown in Scheme I. The reports^{3,6} which describe formation of optically active alcohol 3 are apparently in error. The optical activity which they observed in alcohol 3 was likely due to optically active impurities, for, if the alcohol 3 is rigorously purified, it is found to be optically inactive.