cis-2-Oxa-3a,7a-dihydroindane (*cis*-3a,7a-Dihydrophthalan)

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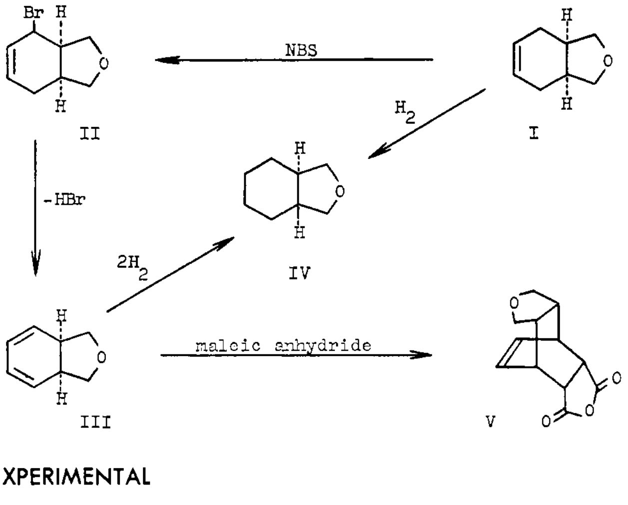
DURING a recently reported investigation into the action of lithium aluminum hydride on a number of cyclic allylic bromides, *cis*-2-oxa-4-bromo-3a,4,7,7a-tetrahydroindane (II) was prepared by the reaction between *N*-bromosuccinimide and *cis*-2-oxa-3a,4,7,7a-tetrahydroindane(I) (*6*). This new allylic bromide was discovered to dehydrobrominate readily under the influence of heat alone to an unknown diolefin as one decomposition product. The same diolefin results, but in better yield, on heating the allylic bromide with quinoline. It was conceivable for this diene to be either of two isomers, *cis*-2-oxa-7,7a-dihydroindane or *cis*-2-oxa-3a,7a-dihydroindane(III). However, from mechanistic considerations it was suspected to be the latter. This paper presents proof that the compound is *cis*-2-oxa-3a,7a-dihydroindane.

The structure of this diolefin has been deduced from these data: the extreme ease with which it adds maleic anhydride; its uptake of two molecular equivalents of hydrogen to form *cis*-2-oxahexahydroindane (IV), identical with the compound produced by the reduction of compound I with one equivalent of hydrogen; characteristic features in its infrared spectrum; and its ultimate analysis. Examination of the nuclear magnetic resonance spectra of the diolefin and its maleic anhydride adduct afforded the final confirmatory evidence for structure III.



EXPERIMENTAL

A Research Specialties Model 60–31 dual-column gas chromatograph was used for the gas-liquid chromatographic analyses. The purification of compound III was performed with an Aerograph Autoprep Model A-700 automatic preparative gas chromatograph. Infrared spectra were determined on a Beckman IR-5 spectrophotometer; absorptions are recorded in wave lengths (μ). The NMR spectra were obtained with a Varian Model A-60 spectrometer at 60 Mc.; chemical shifts are expressed in τ-units relative to tetramethylsilane as internal standard. Elemental analyses were made by the Clark Microanalytical Laboratory, Urbana, Ill.

cis-2-OXA-3a,7a-DIHYDROINDANE (*cis*-3a,7a-DIHYDROPHTHALAN)

Fifteen grams (0.074 mole) of *cis*-2-oxa-4-bromo-3a,4,7,7a-tetrahydroindane (II), [b.p. 68–69° (1 mm. of Hg)] (*6*), 50 ml. of anhydrous quinoline, and 0.5 gram of hydroquinone (polymerization inhibitor) were placed in the pot of a simple vacuum distillation apparatus, and the mixture was gradually heated in an oil bath to 140°. At that point, the pressure within the system was lowered to 30 mm. of Hg, and a colorless distillate collected. This product was washed with dilute sulfuric acid and dried over potassium carbonate. Distillation yielded 7 grams of a fraction boiling at 98° (21 mm. of Hg) which GLC analysis at 145° (1/4 × 144 inch column packed with 10% Carbowax 6000 and 1% silver nitrate supported on 30 to 60-mesh Chromosorb P) revealed to be a mixture containing 77% of diolefin III, 18% of monoolefin I (probably unbrominated starting material), and two unidentified substances (5% of the mixture). Pure III was separated from this mixture by GLC at 100° (3/8 × 240 inch column packed with 20% Carbowax 20M supported on 60 to 80-mesh Chromosorb W). The purified diolefin is relatively unstable toward storage, particularly in the presence of light and air, as evidenced by increase in refractive index and progressive yellowing, n_D^{25} 1.5095. Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.77; H, 8.50.

The infrared spectrum (neat, 0.0212 mm.) exhibited absorption for C=C, conjugated, at 6.30 (m), and for a cyclic ether (*1*) at 9.28 (s). For compound I, the stretching absorption of the lone olefinic bond was observed at 6.02 (m), and that of the cyclic ether moiety at 9.18 (s); in compound IV, the ether absorption was found at 9.23 (s).

NMR data (11% in carbon tetrachloride) showed the following: multiplet at 4.28 (4 vinyl protons); two equal multiplets at 5.91 and 6.52 (4 protons *ortho* to oxygen); and a multiplet at 7.07 (2 angular protons).

DIELS-ALDER ADDUCT OF III WITH MALEIC ANHYDRIDE (V) (1,3-DIOXO-2,6-DIOXAPERHYDRO-4,8-ETHENO-*s*-INDACENE)

The structural formula of this adduct as diagrammed, with both heterocyclic rings *endo* to the etheno bridge, represents the most likely configuration, and as no stereochemical investigation of the compound was attempted, this configuration may be open to question. To 25 ml. of a benzene solution containing 4.0 grams (0.041 mole) of freshly recrystallized maleic anhydride was added 2.8 grams (0.023 mole) of compound III. The solution developed a transient greenish coloration, evolved heat, and a white solid precipitated. The reaction mixture was then warmed under reflux for an hour, cooled, and the precipitate collected by filtration. Concentration of the mother liquor produced an additional amount of the precipitate for a combined yield of 4.6 grams (92%). Gas-liquid chromatographic analysis (employing the silver nitrate-Carbowax 6000 column) showed no III in the final filtrate, demonstrating the quantitative nature of this reaction. A similar attempt to prepare the Diels-Alder adduct of compound III with tetracyanoethylene failed. Apparently, an unstable π-complex did form however, since the reaction mixture assumed a persistent coloration, first red then brownish yellow, but only starting materials could be isolated. Recrystallization from ethanol gave the purified adduct (V) as fine, white needles, m.p. 227–229° (uncorr.). Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49; O, 29.06. Found: C, 65.47; H, 5.36; O, 28.87.

The infrared spectrum (see paragraph on infrared spectrum in section above) (potassium bromide wafer, 4 mg. per 200 mg.) exhibited C=C absorption at 6.08 (w), the cyclic ether band at 9.25 (s), as well as the components of the cyclic anhydride grouping characterized (*2*) by the broad, very strong absorptions of the carbonyl (doublet) at 5.40 to 5.65, and the C—O—C linkage centered at 8.20.

NMR data (10% in trifluoroacetic acid) showed these peaks: triplet at 3.47, 3.56, and 3.64 (2 vinyl protons); a multiplet between 5.74 and 6.43 (4 protons *ortho* to oxygen); a broad peak at 6.56 (4 protons at bridgehead and anhydride ring); and a multiplet at 7.18 (2 angular protons).

cis-2-OXAHEXAHYDROINDANE (*cis*-HEXAHYDROPHTHALAN)

A. From the Hydrogenation of Diolefin III. One gram of III in 1 ml. of ethanol was shaken with 100 mg. of 5% palladized charcoal catalyst for 3 hours at room temperature under 25 p.s.i.g. hydrogen pressure. Two equivalents of hydrogen were taken up. The catalyst was removed by filtration, washed with ethanol, and the combined filtrate and washings were fractionated. One gram of compound IV was obtained, b.p. 51° (8 mm. of Hg), n_D^{21} 1.4701, n_D^{25} 1.4683, d_4^{25} 0.9724 [lit. (*4, 5*) b.p. 59° (9 mm. of Hg), 179° (740 mm. of Hg), n_D^{21}1.4712, n_D^{25}1.4683, d_4^{25} 0.9727].

B. From the Hydrogenation of Monoolefin I. Ten grams of compound I, prepared by the method of Eliel and Pillar (*3*) b.p. 66.0–66.5° (13.5 mm. of Hg), n_D^{25} 1.4890 [lit. (*3*) b.p. 63–64° (13 mm. of Hg), n_D^{25} 1.4884], in 5 ml. of ethanol were hydrogenated in the same manner described for compound III; one equivalent of hydrogen was absorbed. Nine grams of IV were recovered, b.p. 51.5° (9 mm. of Hg), n_D^{26}1.4680, d_4^{25} 0.9733.

The infrared spectra (neat, 0.0212 mm.) of the product derived from method *A* and method *B* were superimposable and corresponded with that of a published spectrum (*4*). Also, GLC analysis (¼ × 120 inch column packed with 15% terephthalic acid-terminated Carbowax 20M supported on 60 to 80-mesh Chromosorb W) of a mixture of the two products gave a single peak.

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Refractive Indices of Some Ternary Systems Containing Naphthalene

Binary Solvent Mixtures Among Benzene, Toluene, Ethylbenzene, Carbon Tetrachloride

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Refractive indices have been determined at 25° C. for the ternary systems of naphthalene dissolved in the six solvent pairs from among benzene, toluene, ethylbenzene, and carbon tetrachloride; and for the various binary subsystems. Equations are given relating refractive index to solution composition in mole fraction. The average deviations in the ternary systems, from predicted refractive indices by these equations, range from 2 to 13 $\times 10^{-5}$ units among the systems. Only in the ethylbenzene-toluene-naphthalene and ethylbenzene-benzene-naphthalene ternary systems are deviations randomly distributed.

ANALYSIS, when performed using physical properties dependent upon the concentrations of all system components, grows more complex as the number of components increases. Graphical procedures, commonly used in relating a property to composition in a binary system, are generally not applicable in multicomponent systems. Analytical functions, although often impractical in hand calculations, may be conveniently used in analysis when computer facilities are available. The present work illustrates the latter approach in representing the refractive indices, *n*, of some ternary systems containing naphthalene.

EXPERIMENTAL DATA

Equipment and procedure in determination of *n*, as well as the purity and *n* of the purified reagents, have been