

partially crystallized upon the addition of ether. The ether-insoluble portion was recrystallized from acetonitrile to give 2.0 g. of a mixture of hydroxy acids, m.p. 139–158°.

This mixture was suspended in 300 ml. of benzene, 200 mg. of *p*-toluenesulfonic acid monohydrate was added, and it was stirred and refluxed for 1 hr. using the Dean-Stark apparatus. The benzene solution was extracted with a NaHCO<sub>3</sub> solution which, in turn, was cooled in an ice bath, stirred, and acidified with cold 2 *N* HCl to pH 5.0. The crystalline precipitate was filtered off and dried *in vacuo* at 60° for 16 hr. to give 1.1 g. (16.0%) of *trans* nonlactonizing hydroxy acid XXIII, m.p. 196–197°. Recrystallization from methanol gave analytically pure XXIII, m.p. 199–200°, which was in every respect identical with the previously described sample obtained in the NaBH<sub>4</sub> reduction of the keto acid XXV.

The benzene solution was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated *in vacuo* to give 0.5 g. (8%) of the *trans* chair lactone XXVII, m.p. 163–164°, after recrystalliza-

tion from benzene-hexane. The melting point of the *trans* boat lactone XII was 165–166°. Mixture melting point determination of XII and XXVII gave a strong melting point depression with a m.m.p. of 138–150°:  $\lambda_{\max}$  221 m $\mu$  ( $\epsilon$  8650), 278 (2060), and 287 (1850);  $\nu_{\max}^{\text{CHCl}_3}$  1780 cm.<sup>-1</sup> ( $\gamma$ -lactone carbonyl). The infrared spectrum of the *trans* chair lactone XXVII was obviously different from that of the *trans* boat lactone XII.

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>3</sub>: C, 74.39; H, 7.02. Found: C, 74.34; H, 6.72.

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## Rearrangement Reactions of 2-Halo-1-methyl-1-tetralols<sup>1</sup>

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The *cis* isomer of 2-chloro-1-methyl-1-tetralol undergoes rearrangement when treated with methylmagnesium bromide or with silver tosylate to give 2-methyl-1-tetralone. The *trans* isomer of 2-bromo-1-methyl-1-tetralol, however, gives 1-methyl-2-tetralone in a reaction with phenylmagnesium bromide and 1-methylnaphthalene with silver tosylate. An  $\alpha,\beta$ -unsaturated alcohol, 1-methyl-1-hydroxy-1,4-dihydronaphthalene, was also isolated from the latter reaction in a trace amount. The *trans* isomer of 2-bromo-1-methyl-1-tetralol forms an epoxide in alcoholic potassium hydroxide. This epoxide rearranges to 1-methyl-2-tetralone in the presence of sulfuric acid. Mechanisms for the rearrangements are discussed.

The semipinacol rearrangement of  $\beta$ -halohydrin by silver salts<sup>2–4</sup> and by Grignard reagents<sup>4–8</sup> have been the subject of many investigations. When the  $\beta$ -halohydrin is incorporated into an alicyclic ring where freedom of rotation is restricted, the stereochemistry about the C- $\alpha$ -C- $\beta$  bond plays an important role in the determination of migration by competing groups and thus the rearrangement path.

The rearrangement of 2-iodo-1-hydroxy-1,2,3,4-tetrahydronaphthalene with silver nitrate, in which 1-indancarboxaldehyde is the product, has been reported by Tiffeneau<sup>2,3</sup> where ring contraction is the result of benzo migration. The necessity for the migrating group to be *trans* to the leaving group in this type of rearrangement has been demonstrated in the rearrangement reaction of 1-methyl-2-halo-1-cyclohexanol with Grignard reagents.<sup>5,6</sup> The *cis* isomer containing the methyl group *trans* to the leaving halogen rearranges to yield 2-methylcyclohexanone with the migration of the methyl group. The *trans* isomer, however, does not contain the methyl group in a position favorable for migration. Instead, it rearranges to yield 1-acetylcyclopentanone by ring contraction.

The thermal rearrangements of the halomagnesium derivatives of *cis*-2-chloro-1-indanol and *cis*-2-chloro-1-methyl-1-indanol have been shown to yield 1-indanone

and 2-methyl-1-indanone, respectively.<sup>8</sup> The corresponding *trans* compounds afford large amounts of tarry materials.

The 2-halo-1-phenyl-1-tetralol series has also been studied.<sup>4,7</sup> The *cis* isomer of 2-chloro-1-phenyl-1-tetralol, under treatment of either silver tosylate<sup>4</sup> or a Grignard reagent,<sup>4,7</sup> yields 2-phenyl-1-tetralone as the rearranged product. This is a case of migratory competition between the benzo and phenyl groups, which are both in positions favorable to migration. The *trans* isomer undergoes rearrangement to give 1-benzoylindane when treated with a Grignard reagent, but produces 1-phenyl-2-tetralone in its reaction with silver tosylate. As the *trans* isomer does not have a phenyl group in a position favorable to migration, it has been suggested that benzo migration occurs to cause ring contraction in one case while rearrangement through an epoxide intermediate prevails in the other.

The present work describes the rearrangement reactions of 2-halo-1-methyl-1-tetralols in an effort to determine the relative tendency of methyl *vs.* benzo migrations and the stereochemical requirements for rearrangement in this special semipinacol system.

### Results

The *trans* isomer of 2-bromo-1-methyl-1-tetralol (I) and the *cis* isomer of 2-chloro-1-methyl-1-tetralol (VIII) were synthesized by employing reactions of known stereochemistry which had been found successful in the production of their phenyl analogs.<sup>4</sup> The *trans*-bromohydrin formed an epoxide IV in alcoholic potassium hydroxide, thus establishing the *trans* configuration of the bromohydrin. This epoxide rearranged to 1-methyl-2-tetralone (II) in the presence of

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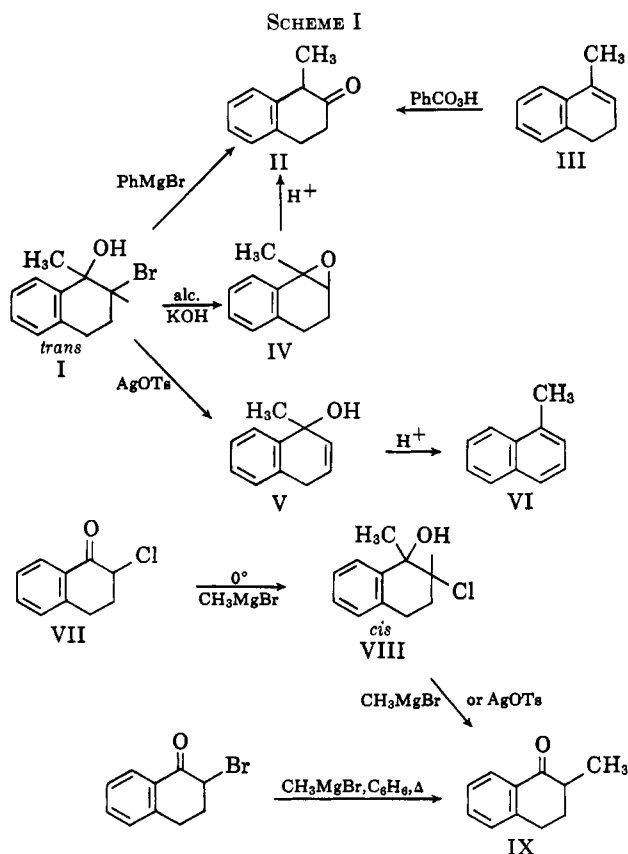
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sulfuric acid (Scheme I). The preparation of *cis*-2-chloro-1-methyl-1-tetralol by the action of methylmagnesium bromide on 2-chloro-1-tetralone (VII) is very sensitive to rearrangement.<sup>7</sup> Careful decomposition of the bromomagnesium salt of the *cis*-chlorohydrin in an ice-cold dilute acid solution led to the isolation of the *cis* compound essentially free of rearranged impurities. The synthesis of *cis*-2-bromo-1-methyl-1-tetralol by the treatment of 2-bromo-1-tetralone with either methylmagnesium bromide or methyl lithium gave crude mixtures which could not be resolved into their pure components by usual purification methods. When the Grignard reaction mixture of 2-bromo-1-tetralone and methylmagnesium bromide was heated at the reflux temperature of benzene for 2 hr., only the rearranged product, 2-methyl-1-tetralone (IX), was isolated in good yield.

The *cis*-chlorohydrin VIII rearranged upon treatment with either methylmagnesium bromide or silver tosylate to give 2-methyl-1-tetralone (IX). The structure of this compound was established by a comparison of the semicarbazone with that of the ketone prepared from 2-bromo-1-tetralone and methylmagnesium bromide at the reflux temperature of benzene. The position of the carbonyl absorption maximum in the infrared region ( $1690\text{ cm.}^{-1}$ ) also serves to substantiate the structure of a conjugated ketone.<sup>4</sup>

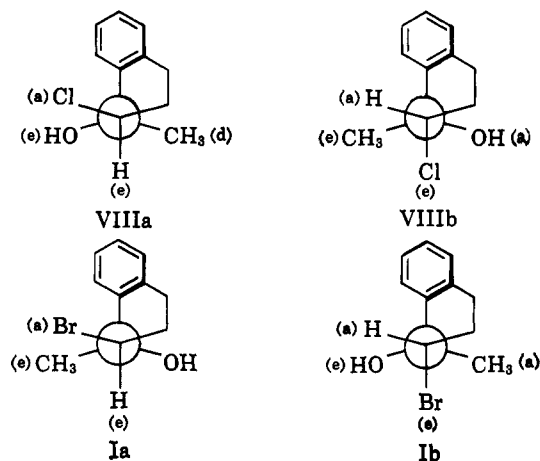
The *trans*-bromohydrin I rearranged upon treatment with phenylmagnesium bromide to give 1-methyl-2-tetralone (II). The structure of this compound was established by independent synthesis from 1-methyl-3,4-dihydronaphthalene and perbenzoic acid.<sup>4,9,10</sup>

The reaction of the *trans*-bromohydrin I with silver tosylate in acetonitrile yielded two isolable products. The major product of this reaction, a  $\text{C}_{11}\text{H}_{10}$  compound, was 1-methylnaphthalene (VI).<sup>11</sup> The structure of this compound was established by the fact that it yielded 1-naphthoic acid upon oxidation with potassium permanganate<sup>12</sup> and the fact that it gave an identical ultraviolet spectrum with an authentic sample of 1-methylnaphthalene. Another product, a  $\text{C}_{11}\text{H}_{12}\text{O}$  compound isolated only in a minor amount, showed two absorption maxima in the infrared region (O-H stretching at  $3640$  and C=C stretching at  $1635\text{ cm.}^{-1}$ ). This unsaturated alcohol was therefore assigned the structure 1-methyl-1-hydroxy-1,4-dihydronaphthalene (V), possibly the actual intermediate in the reaction that led to the formation of 1-methylnaphthalene.

The reaction of 1,2-epoxy-1-methyl-1,2,3,4-tetrahydronaphthalene (IV) with sulfuric acid yielded 1-methyl-2-tetralone (II), the same product obtained by treatment of the *trans*-bromohydrin I with phenylmagnesium bromide.

### Discussion

The *cis*-chlorohydrin VIII could exist in two half-chair conformations. One of these, containing the chlorine and the methyl group in axial positions (VIIIa), should favor the migration of the methyl group. The other conformation, containing the chlorine in the equatorial position (VIIIb), should favor the benzo migration.



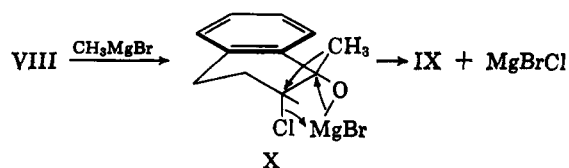
The rearrangement of *cis*-2-chloro-1-methyl-1-tetralol (VII) with methylmagnesium bromide may be explained by an initial attack by the Grignard reagent on the active hydrogen of the chlorohydrin to form the bromomagnesium derivative X. This bromomagnesium derivative could undergo rearrangement according to a cyclic mechanism<sup>8</sup> to afford 2-methyl-1-tetralone (IX). While the same cyclic mechanism might also be proposed for the benzo migration, it can be shown by models that a cyclic intermediate favoring benzo migration would suffer considerable crowding by the axial hydrogen on C-3 of the tetralin skeleton. The

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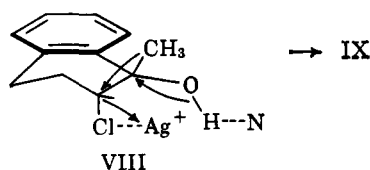
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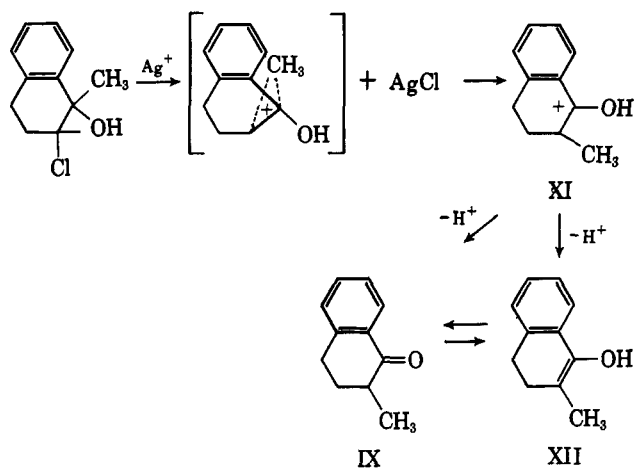


cyclic intermediate favoring methyl migration (XIV) would therefore be energetically favored.

In the rearrangement of *cis*-chlorohydrin VIII with silver tosylate, the migration of the methyl group could also take place by a concerted mechanism in which the ionization of chlorine and the migration of the methyl group were accompanied simultaneously by the removal of a proton by a nucleophile. Alternatively, the first step of the rearrangement may involve

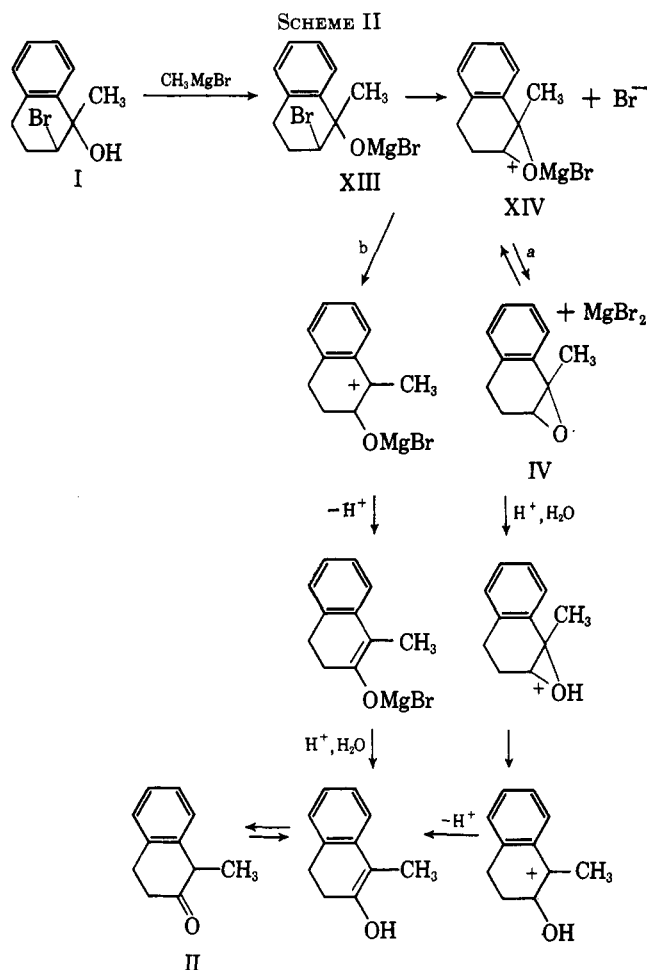


the ionization of the chloride ion with some anchimeric assistance from, or simultaneous migration of, the methyl group to form a carbonium ion intermediate XI. Subsequent loss of a proton by this ionic intermediate could produce the rearranged ketone IX directly or the enol XII.



The *trans*-bromohydrin I also may exist in two possible half-chair conformations. One of these conformations, the one in which the bromine is in an equatorial position (Ib), should favor migration by the benzo group. The other conformation, in which both the bromine and the hydroxyl group are in axial positions (Ia), should favor neither the migration of the methyl group nor the migration of the benzo group.

The rearrangement of this *trans*-bromohydrin (I) with phenylmagnesium bromide again demonstrated the participation of the conformation corresponding to an axial halogen (Scheme II). The initial step in this rearrangement conceivably involved the formation of a bromomagnesium derivative (XIII) of the *trans*-bromohydrin. It is known that, in lieu of a cyclic intermediate, such a halomagnesium derivative may undertake another course of rearrangement action through internal displacement. A nucleophilic attack of the oxygen atom upon the carbon atom to which the bromine was attached would lead to the formation



of an oxonium ion (XIV). Rearrangement of this oxonium-ion intermediate (XIV) *via* either path a or path b would give 1-methyl-2-tetralone (II) as the rearranged product.

In the study of bimolecular nucleophilic substitutions it has been found that, in certain cases, elimination could also take place with relatively nonbasic nucleophiles such as a halide ion or a perchlorate ion.<sup>13</sup> Thus, 2-bromo-2-benzyl-1-tetralone was converted by morpholine at room temperature to 2-benzyl-1-naphthol.<sup>14</sup> A merged substitution-elimination mechanism was proposed in which the attack of the nucleophile was diverted to a  $\beta$ -hydrogen to yield an  $\alpha,\beta$ -unsaturated 2-benzyltetralone as an intermediate. This intermediate readily underwent aromatization under either acidic or basic conditions.<sup>15</sup> Such a reagent as silver nitrate in ethanol has also been found to be an effective dehydrohalogenation agent.<sup>16</sup> It was suggested that the stereochemical facilitation by the conformation in which the bromine was in the axial position was important for the facile *trans*-2,3-diaxial loss of hydrogen bromide to form the  $\alpha,\beta$ -unsaturated ketone.

The reaction of *trans*-bromohydrin I with silver tosylate could be explained by an initial silver-catalyzed elimination of hydrogen bromide from I to yield an

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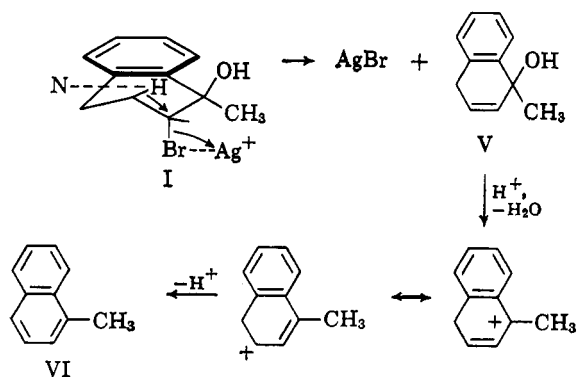
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$\alpha,\beta$ -unsaturated alcohol (V). While this elimination might be a simple metal-catalyzed E1 type of reaction, the ionization of the bromine as bromide ion could also be assisted by the electron pair of the axial C- $\beta$ -H bond. This bond conceivably could have been weakened by a nucleophile such as the tosylate ion, so that the reaction may again be governed by a concerted mechanism. Since a by-product of the elimination reaction was *p*-toluenesulfonic acid, the  $\alpha,\beta$ -unsaturated alcohol V could easily undergo aromatization in such an acidic medium to yield 1-methylnaphthalene.

It is worthwhile to note that Geissman<sup>8</sup> had attempted to affect a semipinacol rearrangement of *trans*-2-chloro-1-methyl-1-indanol with Grignard reagent, but reported the product to be mostly tarry materials. Such difficulty was attributed to polymeri-



zation following a first-order elimination of hydrochloric acid. It should be interesting to observe the difference made by one extra methylene group in the saturated ring. The *trans* isomer of 2-bromo-1-methyl-1-tetralol in the current study had experienced no polymerization difficulty apparently because the carbon skeleton in a tetralin system allowed the formation of an aromatic naphthalene compound as a convenient alternative to the formation of polymers. The indane analogs were not so fortunate because their structural makeup provides no such escape, and consequently, they fell prey to polymerization under the reaction conditions.

It appears that there is an internal consistency in all of the rearrangement reactions of the 2-halo-1-methyl-1-tetralols studied in that the  $\beta$ -halohydrins reacted in the half-chair conformations corresponding to an axial halogen. It is evident that in these rearrangement reactions stereochemistry plays an important part in determining the rearrangement path.

### Experimental<sup>17</sup>

***trans*-2-Bromo-1-methyl-1-tetralol (I).**—A solution was prepared by mixing 35.0 g. (0.25 mole) of *N*-bromoacetamide, 250 ml. of distilled water, 7 ml. of concentrated sulfuric acid, and 35 ml. of *t*-butyl alcohol. This solution was added with vigorous stirring in large doses to a suspension of 350 g. (0.24 mole) of 1-methyl-3,4-dihydronaphthalene in 100 ml. of *t*-butyl alcohol and 55 ml. of water. The reaction mixture was stirred for an additional 11 hr. at 0° in a dark room. The white crystalline solid which separated and settled to the bottom of the flask was re-

moved and washed with cold pentane several times. Recrystallization of the solid bromohydrin I from pentane gave 32.0 g. (30.2%) of product, m.p. 53–54°. The infrared spectrum of the compound showed a sharp peak at 3580 cm.<sup>-1</sup> (OH).

*Anal.* Calcd. for C<sub>11</sub>H<sub>13</sub>BrO: C, 54.77; H, 5.40. Found: C, 54.88; H, 5.44.

***cis*-2-Chloro-1-methyl-1-tetralol (VIII).**—This compound was prepared by the addition of methylmagnesium bromide to 2-chloro-1-tetralone<sup>7</sup> at 0°. It was necessary to filter the bromomagnesium salt of the *cis*-chlorohydrin from the reaction mixture before decomposing it carefully in equal volumes of ice and 5% hydrochloric acid. This produced a crude product essentially free of carbonyl impurities. Failure to do so resulted in the presence of appreciable ketonic impurities in the desired product. It was impossible to purify this crude product by distillation as the *cis*-chlorohydrin VIII apparently underwent a thermal rearrangement<sup>18</sup> as shown by a decrease in the hydroxyl absorption and an increase in carbonyl absorption in the infrared spectrum of the distillate when compared to the spectrum of the crude product before distillation. Fractional freezing of the crude oil from pentane at -80° gave 0.81 g. (16%) of *cis*-2-chloro-1-methyl-1-tetralol (VIII): m.p. -41 to -39°, *n*<sub>D</sub><sup>20</sup> 1.5610. The infrared spectrum of the compound showed an absorption maximum at 3490 cm.<sup>-1</sup> (OH) and no absorption at all in the carbonyl region.

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>ClO: C, 67.17; H, 6.62. Found: C, 66.80; H, 6.82.

**2-Methyl-1-tetralone (IX).**—This compound was prepared by adding an ethereal solution of methylmagnesium bromide to a solution of 2-bromo-1-tetralone<sup>19</sup> in dry benzene. The reaction mixture was heated at the reflux temperature of benzene for 2 hr. to afford 1.5 g. (52%) of 2-methyl-1-tetralone (IX): b.p. 120° (8 mm.), *n*<sub>D</sub><sup>20</sup> 1.5605; lit.<sup>10</sup> b.p. 98° (3 mm.), *n*<sub>D</sub><sup>20</sup> 1.5585. This ketonic product did not give a positive iodoform test. The semicarbazone of the product melted at 200–201° dec. (lit.<sup>10</sup> m.p. 199°). The infrared spectrum of the compound showed an absorption maximum at 1690 cm.<sup>-1</sup>, typical of a conjugated carbonyl in the tetralone system.<sup>4</sup>

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O: C, 82.50; H, 7.50. Found: C, 82.63; H, 7.56.

#### Rearrangement of *cis*-2-Chloro-1-methyl-1-tetralol (VIII).

**A. With Methylmagnesium Bromide.**—A Grignard solution made of an excess of methyl bromide and 0.84 g. (0.035 g.-atom) of magnesium in 50 ml. of anhydrous ether was added to a stirred solution of 4.5 g. (0.023 mole) of *cis*-2-chloro-1-methyl-1-tetralol (VIII) in 40 ml. of dry benzene. The reaction mixture was heated to maintain a gentle refluxing rate for 2 hr. After cooling to room temperature, the mixture was decomposed with 100 g. of ice and 2.2 ml. of concentrated hydrochloric acid. The product was extracted with ether, washed with 5% sodium bicarbonate and water, and dried. The yield of 2-methyl-1-tetralone (IX) which distilled at 91° (2 mm.) was 1.52 g. (41.3%), *n*<sub>D</sub><sup>20</sup> 1.5595. The product did not give a positive iodoform test. The semicarbazone of the product (m.p. 200–201° dec.) showed no melting point depression when mixed with a sample of the semicarbazone of 2-methyl-1-tetralone prepared by treating 2-bromo-1-tetralone with methylmagnesium bromide at the reflux temperature of benzene for 2 hr. The infrared spectrum of the product showed an absorption maximum at 1690 cm.<sup>-1</sup>.

**B. With Silver Tosylate.**—A clear solution of 4.80 g. (0.018 mole) of silver tosylate<sup>20</sup> in 150 ml. of acetonitrile was added in the dark to a stirred solution of 3.31 g. (0.017 mole) of *cis*-2-chloro-1-methyl-1-tetralol in 30 ml. of acetonitrile. The reaction mixture was maintained at the reflux temperature for 7 hr. in the dark. After the removal of silver chloride by filtration, the filtrate was poured into 1.5 vol. of water. The product was extracted with ether, washed with 5% sodium bicarbonate and water, and dried over anhydrous magnesium sulfate. The yield of 2-methyl-1-tetralone which distilled at 99–100° (3 mm.) was 0.8 g. (29.4%), *n*<sub>D</sub><sup>20</sup> 1.5598. The semicarbazone of the product (m.p. 200–201° dec.) showed no melting point depression when mixed with a sample of semicarbazone prepared from the rearrangement product of *cis*-chlorohydrin VIII with methylmagnesium bromide. The infrared spectrum of this compound also showed an absorption maximum at 1690 cm.<sup>-1</sup>.

(17) The infrared spectra were obtained from a Perkin-Elmer Model 21 recording spectrophotometer or a Perkin-Elmer Model 347 Infracord spectrophotometer. Ultraviolet spectra were obtained from ethanolic solutions of the compounds in quartz cells.

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**1-Methyl-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (IV).**—To a solution of 0.450 g. (0.008 mole) of potassium hydroxide in 5 ml. of methanol was added a solution of 1.670 g. (0.007 mole) of *trans*-2-bromo-1-methyl-1-tetralol (I) in 6 ml. of methanol. A precipitate appeared in about 5 min. The reaction mixture was stirred for 2.25 hr. The clear methanolic solution was decanted and the solid was washed with anhydrous ether. The combined organic layer was concentrated under reduced pressure to give a solid material. Two crystallizations of the solid material from pentane gave 0.89 g. (80%) of the epoxide IV, m.p. 34–36°. The infrared spectrum of the compound indicated the loss of a hydroxyl group.

*Anal.* Calcd. for  $C_{11}H_{12}O$ : C, 82.50; H, 7.50. Found: C, 81.74; H, 7.25.

**1-Methyl-2-tetralone (II).**—The reaction of perbenzoic acid with 1-methyl-3,4-dihydronaphthalene in ether<sup>10</sup> gave a 31.5% yield of 1-methyl-2-tetralone (II): b.p. 125° (10 mm.),  $n_D^{20}$  1.5595; lit.<sup>10</sup> b.p. 105–107° (3 mm.),  $n_D^{20}$  1.5495. The infrared spectrum of the compound showed a maximum at 1710  $cm^{-1}$  which was attributed to an unconjugated carbonyl group. This compound gave a negative iodoform test, and its semicarbazone melted at 193–193.5° dec. (lit.<sup>10</sup> m.p. 194° dec.).

*Anal.* Calcd. for  $C_{11}H_{12}O$ : C, 82.50; H, 7.50. Found: C, 82.99; H, 6.55.

**Rearrangement of 1-Methyl-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (IV) with Sulfuric Acid.**—This reaction was carried out according to the procedure reported for the rearrangement of 1,2-epoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene with sulfuric acid.<sup>4</sup> The reaction mixture was heated at reflux temperature for 6 hr. The semicarbazone (m.p. 192–193° dec.) of the crude product showed no melting point depression when mixed with a sample of semicarbazone of 1-methyl-2-tetralone (II) obtained from the reaction of perbenzoic acid with 1-methyl-3,4-dihydronaphthalene (III).

**Rearrangement of *trans*-2-Bromo-1-methyl-1-tetralol (I). A. With Phenylmagnesium Bromide.**—A Grignard solution prepared from 1.20 g. (0.047 g.-atom) of magnesium and 6.5 ml. (7.38 g., 0.047 mole) of bromobenzene in 45 ml. of dry ether was added rapidly to a solution of 11.4 g. (0.047 mole) of *trans*-2-bromo-1-methyl-1-tetralol (I) in 40 ml. of dry benzene. The reaction mixture was heated under nitrogen at the reflux temperature for 6 hr. before it was decomposed on 250 g. of ice covered with 10 ml. of concentrated hydrochloric acid. The product was extracted with ether, washed with 5% sodium bicarbonate solution and with water, and dried over anhydrous sodium sulfate. The yield of 1-methyl-2-tetralone which distilled at 125° (10 mm.) was 2.31 g. (40%),  $n_D^{20}$  1.5615. The infrared spectrum of the product was similar to that of the 1-methyl-2-tetralone obtained from the reaction of perbenzoic acid with 1-methyl-3,4-dihydronaphthalene, both showing a strong maximum at 1710  $cm^{-1}$  (C=O). The semicarbazone (m.p. 192–193° dec.) did not depress the melting point of a sample of semicarbazone of the

ketonic product (II) obtained from the perbenzoic acid reaction. In addition, this compound did not give a positive iodoform test.

*Anal.* Calcd. for  $C_{11}H_{12}O$ : C, 82.50; H, 7.50. Found: C, 82.46; H, 7.64.

**B. With Silver Tosylate.**—A solution of 11.8 g. (0.042 mole) of silver tosylate in 55 ml. of acetonitrile was added in the dark dropwise to a stirred solution of 10.0 g. (0.41 mole) of *trans*-2-bromo-1-methyl-1-tetralol in 45 ml. of acetonitrile. The reaction mixture was stirred at room temperature for 12 hr. After the removal of solid silver bromide by filtration, the reaction mixture was poured into 200 ml. of water. The product was extracted with ether, washed with 5% sodium bicarbonate solution and with water, and dried over anhydrous sodium sulfate. Two products were obtained upon distillation. The yield of 1-methylnaphthalene (VI), the major product, which distilled at 64–65° (0.3 mm.) was 2.4 g. (42%);  $n_D^{20}$  1.616; lit.<sup>10</sup> b.p. 110° (12 mm.),  $n_D^{20}$  1.618. The infrared analysis of the compound showed no significant absorption except those which were characteristic of C–H stretching. This compound also gave an absorption spectrum in the ultraviolet region identical with that obtained from an authentic sample of freshly distilled 1-methylnaphthalene. The permanganate oxidation of the compound following usual procedures gave 1-naphthoic acid, m.p. 160–161° (lit.<sup>21</sup> m.p. 160–161°).

*Anal.* Calcd. for  $C_{11}H_{10}$ : C, 92.96; H, 7.04. Found: C, 93.18; H, 6.83.

The minor product of this reaction, which was first isolated by rapid distillation, b.p. 80–120° (0.3 mm.), was a solid at room temperature. Repeated extraction of this crude solid material with boiling pentane followed by cooling the pentane solution in a bath kept at –5° overnight led to the isolation of a white crystalline product. Recrystallization of this material from cyclohexane yielded 40 mg. (0.06%) of a solid, 1-methyl-1-hydroxy-1,4-dihydronaphthalene, m.p. 108–110°. The infrared spectrum of the compound showed two characteristic absorption maxima, one at 3650 (O–H) and the other at 1635  $cm^{-1}$  (C=C).

*Anal.* Calcd. for  $C_{11}H_{12}O$ : C, 82.50; H, 7.50. Found: C, 82.72; H, 6.57.

**Attempted Preparation of *cis*-2-Bromo-1-methyl-1-tetralol.**—Preparations of *cis*-2-bromo-1-methyl-1-tetralol by the addition of methylmagnesium bromide or methyllithium<sup>22</sup> to 2-bromo-1-tetralone without first isolating the alcoholic salt were unsuccessful. Each experimental run gave a crude oil which contained an appreciable amount of ketonic impurities. It was impossible to purify the products by distillation. The Grignard reactions were conducted at 0 and 35°; the reactions employing methyllithium were conducted at –35, –20, 0, 25, and 35°.

(21) N. A. Lange, Ed., "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 599.

(22) H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **54**, 1957 (1932).

## The Rates of Epoxidation of *cis*- $\Delta^4$ -Tetrahydrophthalic Anhydride and of Related *endo*-Methylene Derivatives

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Second-order rate constants for epoxidation with *m*-chloroperbenzoic acid in chloroform have been found to increase in the order: bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (II) < the *exo* isomer III < the corresponding *endo*-N-phenethylimide IV < the *exo*-N-phenethylimide V << *cis*- $\Delta^4$ -tetrahydrophthalic anhydride (I). Field and steric effects satisfactorily account for the results.

An earlier report from these laboratories<sup>1</sup> showed quite conclusively that the  $\beta$ -epoxy<sup>2</sup> derivative forms as the apparently exclusive product of the peracid epoxidation of *cis*- $\Delta^4$ -tetrahydrophthalic anhydride

(I) and as the predominant product of the epoxidation of derived N-substituted imides. This unexpected result<sup>3</sup> was tentatively rationalized in terms of the "equatorial half-boat" conformation as shown for I, which would offer steric hindrance to  $\alpha$  approach of the

(1) A. P. Gray, D. E. Heitmeier, and H. Kraus, *J. Am. Chem. Soc.*, **84**, 89 (1962).

(2)  $\beta$  according to the steroid convention; that is with the epoxy oxygen and the anhydride ring on the same side of the cyclohexane nucleus.

(3) Cf. H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 221 (1959); N. S. Crossley, A. C. Darby, H. B. Henbest, J. J. McCullough, B. Nicholls, and M. F. Stewart, *Tetrahedron Letters*, 398 (1961).