[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Rearrangement Reactions of 1,2-Disubstituted 1-Phenyl-3,4-dihydronaphthalenes[1]

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The *cis*-chlorohydrin of 1-phenyl-3,4-dihydronaphthalene undergoes rearrangement when treated with phenylmagnesium bromide or with silver tosylate to give 2-phenyl-1-tetralone. The *trans*-bromohydrin, however, gives 1-phenyl-2-tetralone in a reaction with silver tosylate and 1-benzoylindan with phenylmagnesium bromide. The *trans*-bromohydrin of 1-phenyl-3,4-dihydronaphthalene forms an epoxide in alcoholic potassium hydroxide. This epoxide rearranges to 1-phenyl-2-tetralone in the presence of sulfuric acid. Mechanisms for the rearrangements are discussed.

The rearrangement of *cis*- and *trans*-2-halo-1-indanols in the presence of Grignard reagents has been reported to give the same product, 1-indanone.[2,3] To account for these observations, it was proposed that the *cis*-isomers underwent the normal pinacol-type rearrangements, but that the *trans*-isomer rearranged by the formation of an epoxide intermediate.[2]

The necessity for the migrating group to be *trans* to the leaving groups in this pinacol-type rearrangement has been demonstrated in rearrangements of *cis*- and *trans*-halohydrins in the cyclohexene series. The *cis*-1-methyl-2-chloro-1-cyclohexanol rearranges in the presence of a Grignard reagent with the migration of the methyl group. The *trans*-isomer, which does not contain the methyl group in a position favorable to migration, rearranges by ring contraction.[2,4,5] Both *cis*- and *trans* - 1,2 - dimethylcyclohexane - 1,2 - diol, however, afford the same product, 1-methylacetylcyclopentane in the rearrangement with sulfuric acid.[6,7] Ring contraction is also observed in the reaction of 2-iodo-1,2,3,4-tetrahydro-1-naphthol with silver nitrate to afford 1-indanyl aldehyde.[8]

Anchimeric assistance by the benzo group has been shown to increase the rates of solvolysis of 1,2-benzocyclenyl-4-tosylates and to give rearrangement with ring expansion of 1,2-benzocyclenyl-3-methyl tosylates.[9] The rearrangement of *cis*-2-chloro-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (I) with phenylmagnesium bromide, however, produces 2-phenyl-3,4-dihydro-1(2H)-naphthaleneone (II)[8] where phenyl migration instead of benzo migration is preferred.[10]

This work describes the rearrangement reactions of 1,2-disubstituted 1-phenyl-3,4-dihydronaphthalenes in an effort to determine the requirements for phenyl *vs.* benzo migrations.

RESULTS

The reaction of 1-phenyl-3,4-dihydronaphthalene (III) with *N*-bromoacetamide in water and *t*-butyl alcohol gave 2-bromo-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (IV) which yielded 1,2-epoxy-1,2,3,4-tetrahydronaphthalene (V) on treatment with alcoholic potassium hydroxide. The epoxide (V) gave the original bromohydrin (IV) in a reaction with anhydrous hydrogen bromide, thus establishing the *trans*-configuration of the bromohydrin.

The bromohydrin (IV) rearranged on treatment with silver tosylate in acetonitrile to give 1-phenyl-2-tetralone (1-phenyl-3,4-dihydro-2(1H)-naphthaleneone) (VI). The structure of the ketone (VI) was established by comparison with a sample of 1-phenyl-2-tetralone (VI) prepared by the oxidation of 1-phenyl-3,4-dihydronaphthalene with perbenzoic acid.[11] The product obtained from the reaction of the *trans*-bromohydrin (IV) with phenylmagnesium bromide was 1-benzoylindan (VII). The structure of this compound was established by an independent synthesis from 1-indancarboxylic acid chloride and phenylmagnesium bromide.[12,13]

The treatment of 1,2-epoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene with sulfuric acid or with phenylmagnesium bromide gave 1-phenyl-2-tetralone (VI), the same product obtained by treatment of the bromohydrin (IV) with silver tosylate.

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[3] B. Tchoubar, *Compt. rend.*, **214**, 117 (1942).

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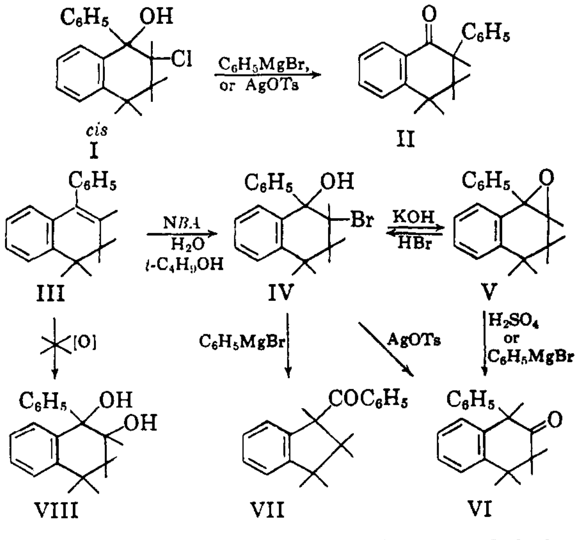
For a comparison of the rearrangement products the *cis*-chlorohydrin, 2-chloro-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (I) was prepared. This compound was reported to yield 2-phenyl-1-tetralone (II) in a reaction with phenylmagnesium bromide.[8] Silver tosylate was also found to be an effective reagent for this conversion.

The rearrangement products (VI, VII) from the *trans*-bromohydrin (IV) and the epoxide (V) were isolated by distillation of the reaction mixtures while the product from the chlorohydrin was obtained by recrystallization. To preclude the possibility that the products obtained by distillation were not formed from a thermal rearrangement or that more than one ketone existed in the reaction mixtures, the infrared spectra of the crude products were compared with the infrared spectra of the pure ketones (II, VI, VII). In all cases the infrared spectra of the crude products indicated that the ketone isolated was the only ketone present in the reaction mixture. The position of the carbonyl peaks in the infrared region also serve to distinguish these isomeric ketones. (II. 1695 cm.$^{-1}$, VI. 1712 cm.$^{-1}$, and VII. 1685 cm.$^{-1}$).

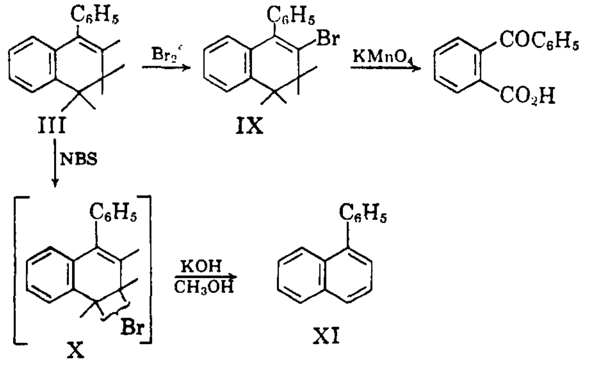
The preparations of *cis*- and *trans*-1-phenyl-1,2,3,4-tetrahydronaphthalene-1,2-diols (VIII) by oxidation of 1-phenyl-3,4-dihydronaphthalene with potassium permanganate,[14] iodine and silver acetate in moist acetic acid[15] and with performic acid[16] were unsuccessful. The reactions gave complex mixtures which could not be resolved into their pure components.



The reaction of 1-phenyl-3,4-dihydronaphthalene (III) with bromine in aqueous and in carbon tetrachloride solutions afforded an unsaturated bromide, $C_{16}H_{13}Br$. The fact that this compound did not react with alcoholic silver nitrate indicated that it was not an allylic or benzylic bromide. Oxidation of the bromide with excess potassium permanganate gave *o*-benzoylbenzoic acid. The reaction of 1-phenyl-3,4-dihydronaphthalene (III) with *N*-bromosuccinimide in carbon tetrachloride[17] gave a product which readily lost hydrogen bromide [probably 3- or 4-bromo-1-phenyl-3,4-dihydronaphthalene (X)] and 1-phenylnaphthalene (XI). Dehydrohalogenation of the unstable bromide afforded 1-phenylnaphthalene. Thus, it was shown that the product from the bromination of 1-phenyl-3,4-dihydronaphthalene with bromine was 2-bromo-3,4-dihydronaphthalene (IX).

DISCUSSION

A study of the models of the *cis*- and *trans*-halohydrins of 1-phenyl-3,4-dihydronaphthalene indicated that each of the isomers could exist in two half-chair conformations. One of the conformations for the *cis*-isomer in which the halide and the phenyl group are in axial positions (XII) should favor the migration of the phenyl group. The other configuration of the *cis*-isomer in which the halide is in an equatorial position (XIII) would favor the migration of the benzo group. The *trans*-isomer may exist in a conformation in which the halide is in an axial position (XIV) and benzo migration would be favored. Neither of the configurations, XIV and XV, however, place the phenyl group in a position *trans*- to the leaving halide group.



In considering the models of the *trans*-halohydrin, the product which would be expected from a normal pinacol-type rearrangement of the *trans*-bromohydrin (IV) would be 1-benzoylindan (VII), *via* the benzonium ion XVI. The *cis*-chlorohydrin (I) could also rearrange to give 1-benzoylindan (VII) through XVI, but only 2-phenyl-1-tetralone is obtained from phenyl migration (XVII).

Either of these products could be accounted for by the formation of the carbonium ion (XVIII) in the rearrangement, but this has been rejected since both the *cis*- and *trans*-halohydrins would then give the same products of rearrangement. The fact that only one product is obtained from the rearrangement of *cis*-2-chloro-1-hydroxy-1-

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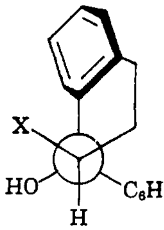
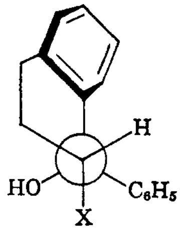
phenyl-1,2,3,4-tetrahydronaphthalene may be accounted for by differences in the migratory aptitudes of phenyl and benzo groups or by differences in the stability of the two conformations (XII and XIII). The possibility of an epoxide intermediate in the rearrangement of the *trans*-bromohydrin to 1-benzoylindan was rejected since only 1-phenyl-2-tetralone (VI) was obtained in the reaction of the epoxide with phenylmagnesium bromide.

The rearrangement of *trans*-2-bromo-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (IV) in the presence of silver tosylate probably occurs by the formation of an epoxide intermediate (XIX), which rearranges to the enol ketone (XXI) by opening the epoxide ring. This may proceed either through the carbonium ion (XX) or by a concerted mechanism (XXII). This same mechanism may be employed to account for the formation of 2-bromo-1-phenyl-3,4-dihydronaphthalene from the bromination of 1-phenyl-3,4-dihydronaphthalene.



XII



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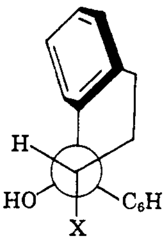
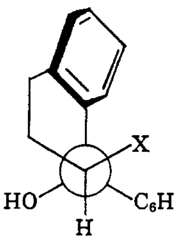
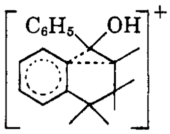


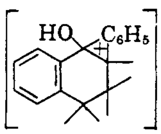
XIV



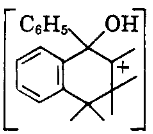
XV



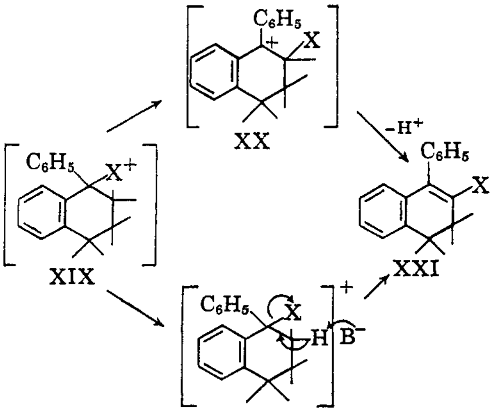
XVI



XVII



XVIII



X = Br or O—H
B = Br or OTs

EXPERIMENTAL[18]

cis-2-Chloro-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (I). This compound was prepared by the addition of phenylmagnesium bromide to 2-chloro-1-phenyl-3,4-dihydro-1(2H)-naphthaleneone, m.p. 97–99° (lit.[10] m.p. 98–99°).

Rearrangement of 2-chloro-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (I) *with silver tosylate.* A solution of 15 g. (0.06 mole) of 2-chloro-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (I) in 100 ml. of dry technical grade acetonitrile was added to 17.3 g. (0.06 mole) of silver tosylate in 100 ml. of acetonitrile, and the mixture was allowed to stand overnight at room temperature. The precipitate which formed was removed by filtration, and the solvent was then removed by distillation at reduced pressure. The residue was extracted with ether and removal of the ether left a solid residue which melted at 65–72°. This residue was recrystallized three times from alcohol and gave 12 g. (92%) of crystalline product which melted at 74–76°. A comparison of this product (mixed melting point and infrared spectra) with a sample of 2-phenyl-1-tetralone (II) obtained from the rearrangement of 2-chloro-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (I) with phenylmagnesium bromide[10,19] showed that they were identical. This compound has an infrared absorption maximum at 1695 cm^{-1}.

2-Bromo-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (IV). This compound was prepared using the procedure reported for the preparation of 1,1-diphenyl-1-hydroxy-2-bromoethane.[20] A stirred suspension of 41.2 g. (0.2 mole) of 1-phenyl-3,4-dihydronaphthalene[21] in 85 ml. of *t*-butyl alcohol and 35 ml. of water was cooled to 0°, and a solution of 32 g. (0.21 mole) of *N*-bromoacetamide monohydrate in 100 ml. of *t*-butyl alcohol and 50 ml. of water was added dropwise over a period of 45 min. The mixture was stirred for an additional 2 hr. at 0°, and the product was precipitated by the addition of 500 ml. of ice water to give 50 g. (83%) of crude product, m.p. 93–95°. Recrystallization twice from 100 ml. of ether at −60° gave an etherate which melted on warming to room temperature and then recrystallized when the ether was removed at reduced pressure. Two additional recrystallizations at −60° from 150-ml. portions of pentane gave 20 g. (33%) of pure white needles of bromohydrin (m.p. 95–96°).

Anal. Calcd. for $C_{16}H_{15}OBr$: C, 63.70; H, 4.90; Br 26.65. Found: C, 63.50; H, 5.10; Br, 26.50.

1,2-Epoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (V). A solution of 4 g. (0.07 mole) of potassium hydroxide in 30 ml. of methanol was added to a stirred solution of 15 g. (0.05 mole) of 2-bromo-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (IV) in 50 ml. of methanol at room temperature.[20] The mixture was then cooled in an ice-salt bath and the solid material was removed by filtration. The product was extracted from the solid material with three 50-ml. portions of ether, and removal of the ether by distillation at reduced pressure yielded a viscous oil. A crystalline product was obtained by cooling the solution of the oil in 100 ml. of pentane to −60°. Recrystallization from pentane gave 9.2 g. (90%) of the product (m.p. 103–104°). The infrared spectrum of the compound showed absorption maxima at 868 $cm.^{-1}$, 1158 $cm.^{-1}$, 1262 $cm.^{-1}$, and 1410 $cm.^{-1}$

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.30. Found: C, 86.03; H, 6.30.

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(18) All melting and boiling points are uncorrected. The infrared spectra were run on a Perkin Elmer Model 21 infrared spectrophotometer.

(19) The authors wish to thank Dr. A. S. Hussey who generously supplied a sample of 2-phenyl-1-tetralone.

(20) S. J. Cristol, J. R. Douglass, and J. S. Meek, *J. Am. Chem. Soc.*, **73**, 816 (1951).

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Treatment of a sample of this compound with anhydrous hydrogen bromide in ether for 3 hr. gave a 91% yield of 2-bromo-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (IV), m.p. 95–96°, which was identical to the original product as shown by mixed melting point and infrared spectra.

1-Indancarboxylic acid. Sufficient 10% sodium hydroxide was added to a mixture of 200 ml. of water and 16 g. (0.1 mole) of 3-indenecarboxylic acid,[12] to dissolve the acid. To this solution was added 200 g. of 3% sodium amalgam. The mixture was stirred for 8 hr., then decanted from the mercury. The solution was acidified with concentrated hydrochloric acid and the product was extracted with ether. The ether was removed by distillation at reduced pressure, and the crude product was recrystallized from hexane to give 12 g. (75%) of the acid melting at 55–58° (lit.[8] m.p. 59–60°). Sublimation of the recrystallized material gave 9.1 g. (56%) of the acid melting at 59–60°.

1-Benzoylindan (VII). To 10 g. (0.062 mole) of 1-indancarboxylic acid was added 33 g. (20 ml., 0.36 mole) of thionyl chloride and 40 ml. of dry benzene.[12] The mixture was allowed to stand for 36 hr. at room temperature and the benzene and thionyl chloride were removed by distillation at reduced pressure. Two additional 100-ml. portions of benzene were added and removed by distillation in order to remove all of the unchanged thionyl chloride. The yellow oily residue from the distillation was dissolved in 100 ml. of benzene and a solution of phenylmagnesium bromide, prepared from 9.8 g. (0.062 mole) of bromobenzene and 1.9 g. (0.08 g.-atom) of magnesium in 100 ml. of anhydrous ether, was added dropwise to the stirred solution of the acid chloride. After the addition was complete, the mixture was heated under reflux for 2 hr. This mixture was then poured over a mixture of 300 g. of ice and 20 ml. of concd. hydrochloric acid. An additional 250 ml. of ether was added, and the mixture was allowed to stand for 2 hr. The ether layer was separated, washed with 5% sodium bicarbonate solution, water, and dried. The ether and benzene were removed and the product was distilled under reduced pressure to yield 7.2 g. (52%) of product; b.p. 120°/.01 mm., n_D^{26} 1.6220.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.53; H, 6.29.

Infrared analysis of the reaction product showed an absorption maximum at 1685 cm.$^{-1}$, (C=O str.). The 2,4-dinitrophenylhydrazone melted at 123–125°.

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.67; H, 4.51. Found: C, 65.59; H, 4.45.

1-Phenyl-3,4-dihydro-2(1H)-naphthalenone. (*1-Phenyl-2-tetralone*) (VI). The reaction of perbenzoic acid with 1-phenyl-3,4-dihydronaphthalene in chloroform followed by treatment of the crude product with sulfuric acid gave a 75% yield of 1-phenyl-2-tetralone, b.p. 120–122°/0.1 mm., n_D^{25} 1.6080. (lit.,[11] b.p. 140–142°/0.5 mm., n_D^{24} 1.6089.) The infrared spectrum showed an absorption maximum at 1712 cm.$^{-1}$ (C=O str.). The phenylhydrazone derivative of the compound melted at 147–148°.

Rearrangement of 2-bromo-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene. (IV) A. *With phenylmagnesium bromide.* To a solution of 15 g. (0.05 mole) of 2-bromo-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (IV) in 100 ml. of dry benzene was rapidly added a solution of phenylmagnesium bromide prepared from 9.5 g. (0.06 mole) of bromobenzene and 2 g. (0.08 g.-atom) of magnesium in 100 ml. of ether. The mixture was heated at reflux temperature for 6 hr. under a dry nitrogen atmosphere. At the end of this time, the reaction mixture was poured over a mixture of 300 g. of ice and 20 ml. of concd. hydrochloric acid. The product was extracted with ether, washed with 5% sodium bicarbonate, water, and the solvent was removed. The yield of 1-benzoylindan (VII) which distilled at 140–146°/0.06 mm. was 4.2 g. (38%), n_D^{26} 1.6224.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.21; H, 6.21.

The infrared spectrum of this compound was identical with the spectrum of a sample of 1-benzoylindan prepared from 1-indancarboxylic acid. A sample of the reaction product was converted to its 2,4-dinitrophenylhydrazone (m.p. 122–125°). A mixed melting point with a sample of the dinitrophenylhydrazone of 1-benzoylindan prepared from 1-indancarboxylic acid chloride was not depressed.

B. *With silver tosylate.* A solution of 27.8 g. (0.1 mole) of silver tosylate in 100 ml. of acetonitrile was added to a solution of 20.2 g. (.067 mole) of 2-bromo-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (IV) at room temperature and allowed to stand overnight. The silver bromide precipitate was removed by filtration and 500 ml. of water was added to the solution. The product was removed from this mixture by extraction with ether. The ether extracts were combined, washed with a 2% sodium bicarbonate solution, water, and dried. The yield of the product which distilled at 120–128°/0.02 mm., n_D^{25} 1.6085, was 9.3 g. (62%). The phenylhydrazone of this product (m.p. 146–148°) showed no change in melting point when mixed with a sample of the phenylhydrazone of the 1-phenyl-2-tetralone (VI) prepared from 1-phenyl-3,4-dihydronaphthalene, and the infrared spectra of the two ketones were identical.

Rearrangement of 1,2-epoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (V) *with sulfuric acid.* To 100 ml. of 30% sulfuric acid was added 2.2 g. (0.01 mole) of 1,2-epoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene. The mixture was refluxed for 3.5 hr., allowed to cool at room temperature, and the product was extracted with ether. The ether solution was washed with a 5% sodium bicarbonate solution, water, and dried. Distillation gave 1.2 g. (54.5%) of the product, b.p. 120–125°/0.01 mm., n_D^{25} 1.6082 whose infrared spectrum was identical with that of 1-phenyl-2-tetralone. The phenylhydrazone of this product was prepared (m.p. 146–148°) and showed no melting point depression when mixed with a sample of the phenylhydrazone of 1-phenyl-2-tetralone.

Rearrangement of 1,2-epoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene (V) *with phenylmagnesium bromide.* A solution of phenylmagnesium bromide, prepared from 5.6 g. (0.036 mole) of bromobenzene and 1 g. (0.04 g.-atom) of magnesium in 100 ml. of ether was added to a solution of 8 g. (0.036 mole) of 1,2-epoxy-1-phenyl-1,2,3,4-tetrahydronaphthalene in 100 ml. of benzene. This mixture was heated under reflux for 6 hr. and poured over a mixture of ice and ammonium chloride. The organic layer was removed, washed with water, and dried. Distillation gave 2 g. (25%) of 1-phenyl-2-tetralone (VI), b.p. 150–155°/0.7 mm., n_D^{27} 1.6110. The phenylhydrazone had a melting point of 147–149° and showed no melting point depression when mixed with an authentic sample. The infrared spectra of the ketone product and 1-phenyl-2-tetralone were identical.

Bromination of 1-phenyl-3,4-dihydronaphthalene (III). A rapidly stirred mixture of 200 ml. of water and 20.5 g. (0.1 mole) of 1-phenyl-3,4-dihydronaphthalene was heated to 70°, and a solution of 16 g. (5.5 ml., 0.1 mole) of bromine in 225 ml. of 10% potassium bromide solution was added slowly. The reaction mixture was maintained at 70° until the bromine was decolorized. The product was extracted from the reaction mixture with benzene, the benzene solution was dried, and the benzene removed by distillation at reduced pressure. The product was a yellow oil which crystallized from methanol to give 20.1 g. (70%) of the crude product which melted at 55–62°. Six additional recrystallizations from alcohol gave 6.0 g. (21%) of white needles which melted at 67–67.5° and did not react with alcoholic silver nitrate. The infrared spectrum of this compound showed an absorption maximum at 1627 cm.$^{-1}$ (C=C conj.).

Anal. Calcd. for $C_{16}H_{13}Br$: C, 67.37; H, 4.59; Br, 28.04. Found: C, 67.35; H, 4.62; Br, 28.41.

This reaction was repeated at 97° and at 90° with 10 g. of sodium bicarbonate added to the water and 1-phenyl-3,4-dihydronaphthalene mixture. The yields of crude product from these reactions were 19 g. (66.2%) and 19.5

g. (68%) respectively. A solution of 10.2 g. (0.05 mole) of 1-phenyl-3,4-dihydronaphthalene in 60 ml. of carbon tetrachloride at 0° was brominated with 8 g. (2.75 ml., 0.05 mole) of bromine in 100 ml. of carbon tetrachloride to give 8 g. (56%) of the same bromide.

A 3-g. (0.01 mole) sample of this compound was treated with 20 ml. of 0.5*N* sodium hydroxide solution, heated on a steam bath, and a solution of 7 g. (0.04 mole) of potassium permanganate in 60 ml. of water was added over a period of 30 min. After the addition was complete, the solution was heated for an additional 24 hr., and 5 ml. of ethyl alcohol was added to destroy any unchanged permanganate. The solution was acidified with 10 ml. of concd. hydrochloric acid and 1 ml. of 6*N* nitric acid. This mixture was then heated for an additional 2 hr. and allowed to cool to room temperature. The product was extracted with ether and washed with sodium hydroxide solution. The sodium hydroxide solution was acidified with concentrated hydrochloric acid and the product was extracted from the water solution with ether. Evaporation of the ether gave 0.9 g. (36%) of a compound, which after drying for 2 days at reduced pressure over phosphorus pentoxide, melted at 122-125°. A mixed melting point with an authentic sample of *o*-benzoyl benzoic acid was not depressed.

The preparation of 3- or 4-bromo-3,4-dihydronaphthalene was attempted by adding 10.7 g. (0.06 mole) of *N*-bromosuccinimide to a solution of 10.7 g. (0.05 mole) of 1-phenyl-3,4-dihydronaphthalene in 100 ml. of dry carbon tetrachloride. The flask was exposed to an ultraviolet lamp, heated to reflux temperature, and a small amount of benzoyl peroxide added to initiate the reaction. After a short induction period, the reaction proceeded violently with the liberation of bromine and hydrogen bromide. The reaction was complete in 6 hr. and the succinimide was removed by filtration. The solvent was removed and the product distilled at reduced pressure to yield a lower boiling fraction (b.p. 175-182°/1 mm.), which had a deep blue color characteristic of azulene. The higher boiling fraction (b.p. 185-195°/1 mm.), was redistilled to afford 2 g. of product containing bromine (b.p. 192°/1 mm.).

Anal. Calcd. for $C_{16}H_{13}Br$: C, 67.37; H, 4.59. Found: C, 69.04; H, 4.04.

A sample of this bromo compound was treated with alcoholic potassium hydroxide to yield 1-phenylnaphthalene. The 4-bromo and 4-nitro derivatives of 1-phenylnaphthalene melted at 68-69° and 128-130°, respectively (lit.[22] m.p. 70° and 132°). The same derivatives were obtained from the low boiling fraction of the reaction product.

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[CONTRIBUTION FROM MELLON INSTITUTE]

The Ozonolysis of Acenaphthylene[1]

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The ozonolysis of acenaphthylene was studied in the participating solvents, methanol and *t*-butyl alcohol. In the case of methanol, the first isolable product was 3-hydroxy-7-methoxy-4,5,6-(1,8-naphtho)-1,2-dioxacycloheptane, which was apparently formed by cyclization of the 8-formyl-1-naphthylmethoxymethyl hydroperoxide previously reported by Criegee. With *t*-butyl alcohol, presumptive evidence for the presence of an analogous uncyclized hydroperoxide was obtained. This hydroperoxide apparently did not cyclize.

The conversion of these primary ozonolysis products to 1,8-naphthalenedialdehyde, 1,8-naphthalic acid, 1,8-naphthaldehydic acid, methyl 8-formyl-1-naphthoate, and 1,8-naphthalide in fair to good yields was also part of this study. The dialdehyde was isolated as the bis(*p*-nitrophenylhydrazone) in 39% yield. Infrared examination of the aldehyde-acid and its methyl ester showed that these compounds exist in lactonic forms rather than as uncyclized compounds.

In his review article on *Organic Peroxides*, Criegee indicated that acenaphthylene (I) on ozonolysis in methanol yielded 8-formyl-1-naphthylmethoxymethyl hydroperoxide (II).[2] Details of this experiment have not been published, but recent studies by Bailey[3] on the ozonolysis of phenanthrene in methanol and by Warnel and Shriner[4] on the ozonolysis of indene in ethanol have demonstrated the presence of analogous hydroperoxides or the cyclic peroxides (hemiperacetals) formed by cyclization of intermediate formyl-alkoxymethyl hydroperoxides.

In the present study, acenaphthylene in methanol at -30° was treated with 1.06 molecular equivalents of ozone. A white crystalline solid was isolated by quickly filtering the cold reaction mixture and washing the solid with cold petroleum ether. The solid melted at 115-116° dec. but gradually decomposed at room temperature.

Assignment of the structure 3-hydroxy-7-methoxy-4,5,6-(1,8-naphtho)-1,2-dioxacycloheptane (III) to this compound was based on (a) a correct elementary analysis, (b) satisfactory analyses for active oxygen and methoxyl, (c) a negative hydroperoxide test,[5] and (d) the absence of a carbonyl band and the presence of a hydroxyl band in the infrared spectrum of the compound.

Structure III is obviously the hemiperacetal formed by cyclization of II as anticipated from the observation of Bailey that alkoxy hydroperoxides

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(1) Presented before the Division of Organic Chemistry, American Chemical Society, 136th Meeting, Atlantic City, N. J., September 17, 1959.

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