in ether, washed with water, dried over sodium sulfate, and distilled. The yield of dimethyliodoarsine boiling at 154–155° was 157 g. or 46%.

3-Quinolyldimethylarsine.—A solution of 26.6 g. (0.12 mole) of dimethyliodoarsine in 200 ml. of ether was added with stirring over a 15-minute period to an ether solution of 0.12 mole of 3-quinolyllithium[7] cooled to −15°. The mixture was stirred for one hour after completion of the addition, hydrolyzed and the ether layer separated and dried. Distillation gave 21 g. (74%) of 3-quinolyldimethylarsine boiling 124–127° at 0.5 mm. pressure.

Anal. Calcd. for $C_{11}H_{12}AsN$: N, 6.01. Found: N, 6.18.

2-(Di-*n*-propylarsinophenyl)-quinoline.—*p*-Bromophenyldi-*n*-propylarsine (39 g. or 0.15 mole) was treated with *n*-butyllithium in the usual fashion for halogen–metal interconversion[8] and the resulting solution of *p*-lithiophenyldi-*n*-propylarsine was added with stirring at 0° over a 30-minute period to a solution of 15.3 g. (0.12 mole) of quinoline in 50 ml. of ether. The reaction mixture was hydrolyzed with water and a few ml. of nitrobenzene added for oxidation of the intermediate dihydro compound. Separation of the ether layer followed by drying over sodium sulfate and distillation gave 26 g. (60%) of product boiling at 218–219° (0.08 mm.).

Anal. Calcd. for $C_{21}H_{24}AsN$: N, 3.83. Found: N, 3.78.

The compounds listed in Table I were prepared in general accordance with the procedures described above.

(7) H. Gilman and S. Spatz, THIS JOURNAL, **63**, 1553 (1941).

(8) R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y.

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The Anomalous Reduction of 7,9-Diketoperinaphthane and its Methyl Ether

BY MARTIN GOLDMAN[1]

RECEIVED NOVEMBER 25, 1953

During recent attempts to synthesize bromoperinaphthene,[2] the reduction of 7,9-diketoperinaphthane (I) was investigated for the purpose of preparing 7,9-dihydroxyperinaphthane (II).

However, instead of the desired alcohol, the isomeric phenol, 1,3-dihydroxyperinaphthane (III), was obtained as the product of the reduction.

Several attempts to reduce 7,9-diketoperinaphthane by means of lithium aluminum hydride in ether or in tetrahydrofuran solution were unsuccessful. Similarly, sodium borohydride in aqueous sodium hydroxide appeared to be without action on the diketone. However, Adams catalyst effected the reduction of I in ethanolic solution to the phenol III. Somewhat more unexpected was the fact that the use of Raney nickel catalyst, which does not ordinarily catalyze the reduction of aromatic nuclei under mild conditions,[3] afforded the same compound in a reduction conducted at room temperature and at atmospheric pressure.

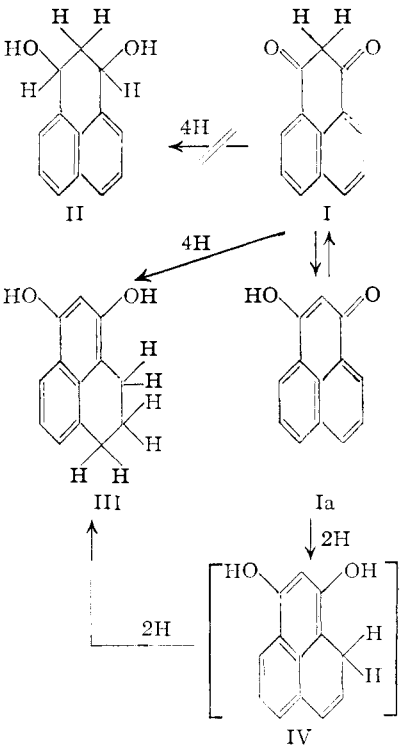
This mode of reduction of the diketone was not completely surprising in view of its existence in the tautomeric form of 9-hydroxyperinaphthenone (Ia). Boekelheide and Larrabee[4] have reported the isolation of a phenolic fraction from the reduction

(1) Beaunit Mills Predoctoral Fellow, 1951–1952. Eastman Kodak Co., Rochester 4, New York.

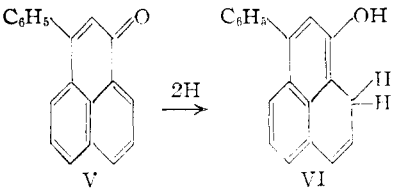
(2) V. Boekelheide and M. Goldman, THIS JOURNAL, **76**, 604 (1954).

(3) H. Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wisconsin, 1937, p. 56 ff.

(4) V. Boekelheide and C. E. Larrabee, THIS JOURNAL, **72**, 1245 (1950).



product of perinaphthenone. Also, Koelsch and Anthes[5] have found that the reduction of 9-phenylperinaphthenone (V) led to a phenolic derivative for which they wrote structure VI.



It appears quite likely that 7,9-diketoperinaphthane reacts in the enol form Ia and the absorption of the first molecule of hydrogen occurs by 1,4-addition to afford 1,3-dihydroxyperinaphthene (IV) corresponding to the phenyl analog VI isolated by Koelsch and Anthes. However, in the present instance, the intermediate perinaphthene absorbed a second molecule of hydrogen to afford, as the final product, 1,3-dihydroxyperinaphthane (III).

Similarly, the reduction of 9-methoxyperinaphthenone (VII) in the presence of Raney nickel or copper chromite catalyst afforded a phenolic product, presumably 1-hydroxy-3-methoxyperinaphthane (VIII). Both 1,3-dihydroxyperinaphthane and its monomethyl ether VIII when treated with dimethyl sulfate in aqueous alkali, afforded the identical dimethyl ether derivative, 1,3-dimethoxyperinaphthane (IX).

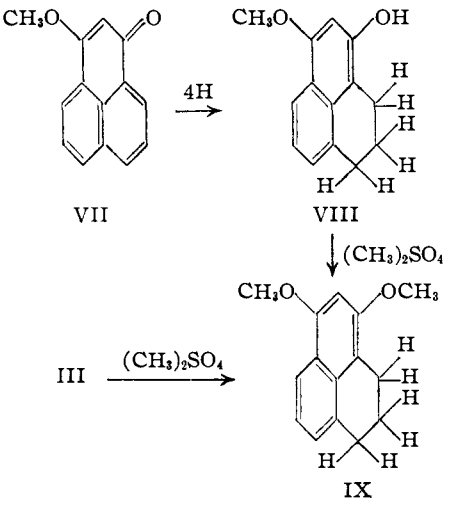
Experimental[6]

7,9-Diketoperinaphthane (I).—The procedure employed was that of Errera.[7] The compound was obtained as a yellow solid, m.p. 250–254° (unrecrystallized) in 89% yield.

(5) C. F. Koelsch and J. A. Anthes, *J. Org. Chem.*, **6**, 558 (1941).

(6) Analyses by Miss Claire King.

(7) G. Errera, *Gass. chem. ital.*, **41I**, 190 (1911).



9-Methoxyperinaphthenone (VII).—7,9-Diketoperinaphthane was alkylated by means of dimethyl sulfate in aqueous sodium hydroxide solution. The product was recrystallized with difficulty from a benzene–heptane solution in the form of brown crystals, m.p. 142–146° (lit.[7] 144°).

Reduction of 7,9-Diketoperinaphthane.—Several attempts to reduce the diketone by means of lithium aluminum hydride in ether or in tetrahydrofuran were carried out by refluxing the hydride solution under a Soxhlet extractor containing the ketone. The only solid isolated from the reaction mixture was the starting material. Similarly, sodium borohydride in aqueous sodium hydroxide appeared to be without action on the diketone.

A suspension of 3 g. of 7,9-diketoperinaphthane in 250 ml. of ethanol was hydrogenated in the presence of Raney nickel at 40 lb. pressure and at room temperature for two hours. The catalyst was removed by filtration, the solution was concentrated over a steam-bath *in vacuo* and diluted with water which precipitated 1.6 g. of tan crystals, m.p. 163–166°. The aqueous filtrate was extracted with ether and the latter solution was concentrated to a small volume and extracted with sodium hydroxide solution. The alkaline solution was cooled in an ice-bath and acidified to yield an additional 1.0 g. of crude product. Recrystallization of the product from benzene–heptane solution (Darco) and finally from a small volume of benzene afforded very light orange crystals, m.p. 167–168.5°. The compound tended to darken and became less pure on further recrystallization. It was insoluble in 10% sodium carbonate solution, but dissolved readily in 10% sodium hydroxide solution.

The same reduction can be effected with Adams catalyst under the same conditions.

Anal. Calcd. for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.64; H, 6.03.

Reduction of 9-Methoxyperinaphthenone.—The use of lithium aluminum hydride in refluxing ether–dioxane or ether–benzene solution failed to effect the reduction of 9-methoxyperinaphthenone.

One-half gram of VII in 35 ml. of methanol absorbed 2 molar equivalents of hydrogen at room temperature and at atmospheric pressure in the presence of 100 mg. of Adams catalyst, the solution was filtered and the filtrate diluted with water. There was obtained 0.4 g. of orange needles, m.p. 115–119°. Two recrystallizations of the solid from cyclohexane–hexane solution yielded pale yellow needles, m.p. 118–120°. Repeated crystallizations using decolorizng agents did not effect any further purification. The compound was insoluble in 10% sodium carbonate solution but soluble in 10% sodium hydroxide solution.

The identical product was obtained when 1 g. of VII in the presence of 0.1 g. of copper chromite catalyst suspended in 10 ml. of methanol was hydrogenated at 100° and at 1300 lb./sq. in. for 1 hour.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59; CH_3O, 14.48. Found: C, 78.80; H, 6.73; CH_3O, 14.00.

Methylation of 1-Hydroxy-3-methoxyperinaphthane.—A solution of 1.2 g. of VIII in 10% sodium hydroxide was treated dropwise with 15 ml. of dimethyl sulfate at room temperature. The solution was maintained alkaline by the addition of more base as required. The insoluble product was filtered and recrystallized several times from aqueous methanol which afforded white crystals, m.p. 69–70°. A polymorphic modification was obtained which melted at 81–84°, and was readily converted to the lower melting form.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07; CH_3O, 27.19. Found: C, 78.77; H, 7.20; CH_3O, 26.96.

Methylation of 1,3-Dihydroxyperinaphthane.—The methylation was carried out as described above for VIII. The product was recrystallized from aqueous methanol and melted at 67–69°. There occurred no depression of the melting point on admixture of this compound with a sample obtained in the preceding experiment. The same polymorphic modifications were obtained in this instance.

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Steric Control of Asymmetric Induction in the *ortho*-Claisen Rearrangement

BY HAROLD HART

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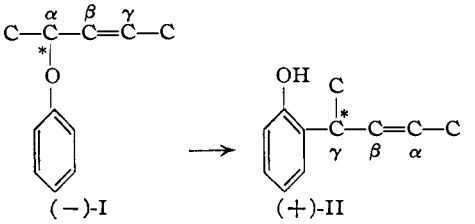
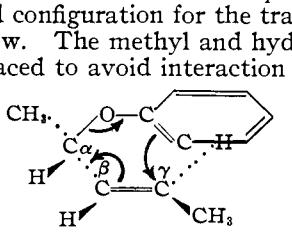
Alexander and Kluiber[1] showed that the Claisen rearrangement of (−)-α,γ-dimethylallyl phenyl ether gave (+)-2-(α,γ-dimethylallyl)-phenol. In



this rearrangement, asymmetry was destroyed at C_α and created at C_γ. But, because of the symmetry of the α,γ-dimethylallyl group, similar moieties are attached to the asymmetric carbon in both the ether and its rearrangement group, *i.e.*, hydrogen, methyl, propenyl and an aromatic group. Alexander and Kluiber suggested that retention of activity was consistent with the established cyclic mechanism proposed for this rearrangement,[2] and that one form of the transition state is preferred over the other because of steric interaction between the methyl on C_α and the hydrogen on C_β. This leads to an asymmetric synthesis.

It is the purpose of this note to make more explicit the explanation of Alexander and Kluiber, and to show that the configuration at C_γ in II will be identical with the configuration at C_α in I. This prediction, based on steric requirements in the transition state, is then substantiated by data taken from Alexander and Kluiber's paper.

A preferred configuration for the transition state is shown below. The methyl and hydrogen on C_α have been placed to avoid interaction between the



(1) E. R. Alexander and R. W. Kluiber, THIS JOURNAL, **73**, 4304 (1951).

(2) See, for example, J. P. Ryan and P. R. O'Connor, *ibid.*, **74**, 5866 (1952).