

tion to the aliphatic value was attained. We have no explanation of this fact.

It was suggested to us by Dr. W. G. Brown that the efficiency of ortho methyl groups in preventing coplanarity, and therefore resonance, should be temperature dependent. The higher the temperature, the more should the blocked-out group (*e. g.*, the acetyl methyl group in acetophenone) be able to force its way for a time into the region occupied by the ortho methyls and thus achieve coplanarity; the moment of the substituted compound should therefore increase with increasing temperature. This experiment was not tried, due to the smallness of the effects expected and to the fact that the solvent influence would, presumably, also change with temperature.

It is to be noted that resonating structures such as II and III should lead to a shortening in length of the bond connecting the —COR group with the ring and to an increase in the ring —C—R angle corresponding to double bond formation between ring and carbonyl carbon. We would also expect that the inhibition of these resonating structures by ortho methyls should tend to increase the bond distance and decrease the angle in question

to the values predicted on the basis of structure I. Unfortunately, the direct determination of these quantities by X-ray or electron diffraction measurements is, as yet, not possible for such complicated molecules.

The authors wish to thank Drs. W. G. Brown and G. W. Wheland and Mr. N. R. Davidson for their kind assistance and many helpful comments during the course of this work.

Summary

1. By the method of Birtles and Hampson it has been shown from dipole moment measurements that the resonance of compounds of the type C_6H_5COR involving quinonoid structures may be inhibited by two ortho methyl groups.

2. This inhibition of resonance is purely a steric effect in which the ortho methyl groups block the attainment of the completely coplanar configuration necessary in the quinonoid structure.

3. The steric effect depends on the size of the —COR group, being absent in the small —CHO group while —COCH₃ and —COCl lead to readily observable effects.

CHICAGO, ILLINOIS

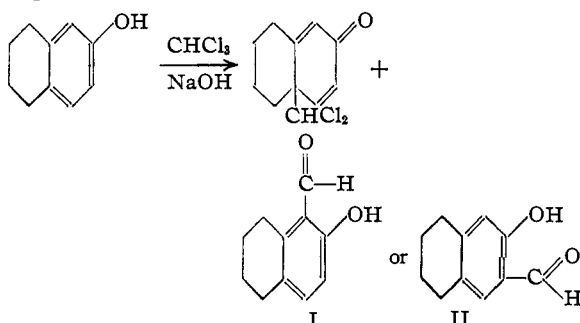
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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reimer-Tiemann Reaction of β -Tetralol

BY RICHARD T. ARNOLD, HAROLD E. ZAUGG AND JOSEPH SPRUNG

In a valuable paper recently published, Woodward¹ made use of the Reimer-Tiemann reaction for the direct introduction of angular groups into polycyclic molecules. The neutral compound from β -tetralol is accompanied by a 50% yield of expected hydroxyaldehyde (*m. p.* 86–87°).²



(1) Woodward, *THIS JOURNAL*, **62**, 1208 (1940).

(2) We are indebted to Dr. R. B. Woodward for a highly purified sample of the aldehyde for purposes of comparison. Its melting point was originally given as 82°.¹

Previous work on the orientation of β -tetralol^{3,4} led to the reasonable assumption that the aldehyde could be correctly formulated as (II).

β -Tetralol yields the same hydroxyaldehyde in the Gattermann synthesis.⁵

Numerous early attempts to prove the structure of the hydroxyaldehyde by direct oxidation or indirect conversion to the hydroxy acid failed.⁵

The importance of these substances to our investigation of the Mills-Nixon problem necessitated a complete proof of structure.

Using the basic fusion method of Kauffmann,⁶ the hydroxyaldehyde was readily transformed into the corresponding acid (V). That the chief product of the Reimer-Tiemann reaction is (I) and not (II) as formerly supposed is proved by the

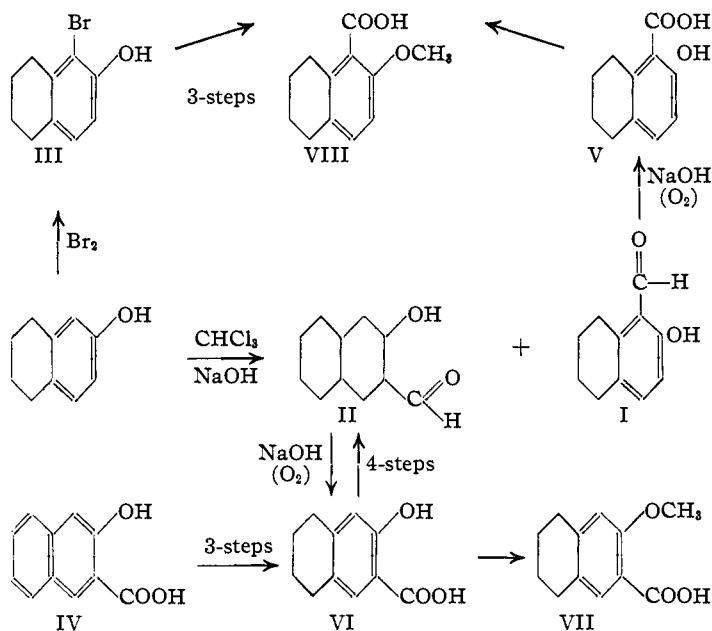
(3) Schroeter, *Ann.*, **426**, 147 (1922).

(4) Robinson and Walker, *J. Chem. Soc.*, 1531 (1935).

(5) Thom and Kross, *Arch. Pharm.*, **265**, 336 (1927).

(6) Kauffmann, *Ber.*, **15**, 806 (1882).

relationship between I and the well-known bromotetralol (III) and an unequivocal synthesis of (II) from 2,3-hydroxynaphthoic acid (IV). Compound (II) was also obtained in minute amounts from the Reimer-Tiemann reaction. The structure of the acid VI (first prepared by Schroeter³) has recently been proved by Robinson and Walker.⁴



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Experimental

Ethyl (1,2,3,4 - Tetrahydro - 6 - hydroxy) - 7 - naphthoate.—One hundred and sixty-seven grams of ethyl 3-hydroxy-2-naphthoate was reduced catalytically with hydrogen and 4–5 g. Raney nickel. The theoretical quantity of hydrogen was taken up in two and one-half hours at 140–150° and a pressure of 900 pounds. The product was distilled *in vacuo*; b. p. 155–161° (4 mm.); yield 94%.

1,2,3,4 - Tetrahydro - 6 - hydroxy - 7 - naphthoic Acid (VI).—Into a three-necked flask fitted with stirrer and condenser and containing 100 g. of sodium hydroxide in one liter of water, at its boiling point, 160 g. of ethyl (1,2,3,4-tetrahydro-6-hydroxy)-7-naphthoate was added with stirring. The sodium salt of the phenol precipitated as a white solid, but after one and one-half hours dissolved. Charcoal was added and the heating continued for an additional thirty minutes. The solution was cooled, filtered, and acidified. After recrystallization from alcohol-water the yield was 125 g. (90%); m. p. 180–182°.³

Preparation of 1,2,3,4-Tetrahydro-6-acetoxy-7-naphthoic Chloride.—To 24 g. of 1,2,3,4-tetrahydro-6-acetoxy-7-naphthoic acid³ dissolved in 100 cc. of dry benzene was added 25 cc. of purified thionyl chloride. The mixture was refluxed for two hours and the excess solvent and thionyl

chloride removed under vacuum. The residual oil solidified on standing. Recrystallization from ether-petroleum ether gave 18 g. of acid chloride; m. p. 90–92°.

Anal. Calcd. for $C_{13}H_{13}O_3Cl$: C, 61.78; H, 5.18. Found: C, 61.96; H, 5.41.

Preparation of 1,2,3,4-Tetrahydro-6-hydroxy-7-naphthaldehyde (II).—In a 125-cc. conical Grignard flask, fitted with an inlet tube extending to the bottom, and connected to a short reflux condenser was placed 12.5 g. of 1,2,3,4-tetrahydro-6-acetoxy-7-naphthoic chloride dissolved in 90 cc. of xylene. Five grams of palladium-on-barium sulfate catalyst was then added and purified hydrogen passed in at such a rate that the catalyst was well stirred. Hydrogen chloride was evolved rapidly at 130°. After four hours the hydrogen chloride evolution slackened considerably but heating was continued for an additional eight hours. The solution was cooled, filtered, and the solvent distilled until the total volume was 25 cc. Extraction with 60 cc. of 2 *N* potassium hydroxide gave a yellow water layer which deposited crystals of a potassium salt on cooling. This material on acidification gave 1.73 g. of hydroxyaldehyde. A second basic extraction gave an additional 1.68 g. of hydroxyaldehyde, m. p. 56–57°.

Anal. Calcd. for $C_{11}H_{13}O_2$: C, 74.96; H, 6.86. Found: C, 75.03; H, 7.02.

This hydroxyaldehyde gave a copper chelate derivative when warmed with a solution of copper acetate. The oxime melted at 105.5–106.5°.

Anal. Calcd. for $C_{11}H_{13}O_2N$: N, 7.32. Found: N, 7.05.

Oxidation of 1,2,3,4-Tetrahydro-6-hydroxy-7-naphthaldehyde.—To eight pellets of potassium hydroxide in a nickel crucible, arranged for heating in a Wood's metal bath, was added enough water to form a paste; to it was added 0.1 g. of analytically pure 1,2,3,4-tetrahydro-6-hydroxy-7-naphthaldehyde, and the bath temperature was slowly raised to 250°. At 220°, foaming began and it became necessary to stir the mixture. At 250°, the melt set to a solid mass, and after heating at this temperature for a few minutes the metal bath was removed. After dissolving the solid mass in water, filtering, and making the solution acidic with hydrochloric acid there was obtained fine white needles of melting point 179–181°. A mixed melting point determination with an authentic sample of 1,2,3,4-tetrahydro-6-hydroxy-7-naphthoic acid proved the identity of the substance.

β -Tetralol.—Forty-five grams of 1,2,3,4-tetrahydro-6-naphthylamine (m. p. 35–36°) was dissolved in a solution of 250 cc. of water and 135 cc. of borofluoric acid (184 g. of H_3BO_3 added to 454 g. of 47% HF). The solution was diazotized at 0° with 21.5 g. of sodium nitrite in 50 cc. of water. The thick suspension was added to a solution of 150 cc. of concd. sulfuric acid in 100 cc. of water and warmed on a steam-bath until the evolution of nitrogen ceased. The resulting β -tetralol was taken up with ether, extracted with dilute sodium hydroxide, acidified, re-

extracted with ether and distilled; b. p. 135° (9 mm.), yield 18 g., m. p. 61–62°.

6-Hydroxy-1,2,3,4-tetrahydro-5-naphthaldehyde (I).—A Reimer–Tiemann synthesis was carried out with 5 g. of β -tetralol, 115 cc. of sodium hydroxide (10%) and 13 cc. of chloroform according to the method of Woodward.¹ Instead of distilling the reaction mixture, it was taken up in the ether, extracted with potassium hydroxide solution, acidified, re-extracted with ether and shaken with a saturated solution of sodium bisulfite. The addition product on decomposition with dilute sulfuric acid gave 1.2 g. of a mixture of isomeric *o*-hydroxyaldehydes. Crystallization from dilute ethanol gave an aldehyde (I) (m. p. 86–87°) identical with a sample kindly sent to us by R. B. Woodward.

From the mother liquor after dilution and several recrystallizations from methanol there was obtained a very small amount of an *o*-hydroxyaldehyde (II) (m. p. 56.5–57.5°) identical with that produced in the Rosenmund reduction described above.

6-Hydroxy-1,2,3,4-tetrahydro-5-naphthoic Acid.—One-half gram of 6-hydroxy-1,2,3,4-tetrahydro-5-naphthaldehyde was fused with potassium hydroxide (4 g. in 1 cc. of water). At the end of five minutes, the bright yellow sodium salt turned to a brown viscous paste. The cooled melt was dissolved in water, filtered, and acidified with hydrochloric acid. The crude hydroxy acid (0.18 g.) formed colorless needles when crystallized from dilute ethanol; m. p. 174–175°. A mixed melting point with an authentic sample of 6-hydroxy-1,2,3,4-tetrahydro-7-naphthoic acid showed considerable depression.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.71; H, 6.30. Found: C, 68.51; H, 6.38.

5 - Bromo - 6 - methoxy - 1,2,3,4 - tetrahydronaphthalene.—Eight grams of 5-bromo-6-hydroxy-1,2,3,4-tetrahydronaphthalene was dissolved in 60 cc. of 2 *N* potassium hydroxide solution and methylated with 4 cc. of dimethyl sulfate. After heating for thirty minutes on the steam-bath, the base, insoluble portion was extracted with ether. The solvent was removed and methanol used for recrystallization; yield, 3.2 g.; m. p. 38–39°.

Anal. Calcd. for $C_{11}H_{12}OBr$: C, 54.77; H, 5.44. Found: C, 54.75; H, 5.44.

6-Methoxy-1,2,3,4-tetrahydro-5-naphthoic Acid.—(a) A Grignard solution was prepared from 3 g. of 6-methoxy-5-bromo-1,2,3,4-tetrahydronaphthalene, 0.4 g. magnesium and 15 cc. ether. A drop of ethyl bromide was needed to start Grignard formation. The ether solution of Grignard reagent was dropped slowly into dry ether into which flowed a sustained stream of carbon dioxide. On decomposition, 1.3 g. of crude acid was obtained which on repeated recrystallization from dilute ethanol and petroleum ether melted at 148–150°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.87; H, 6.84. Found: C, 70.23; H, 6.93.

(b) One-tenth gram of 6-hydroxy-1,2,3,4-tetrahydro-5-naphthoic acid was methylated with 0.15 g. of potassium hydroxide in 2 cc. of water and 0.2 cc. of dimethyl sulfate. The product after recrystallization from ethanol and petroleum ether melted at 147–149°. A mixed melting point determination with another sample from (a) above showed no depression.

Methyl 6-Methoxy-1,2,3,4-tetrahydro-7-naphthoate.—1.0 gram of 6-hydroxy-1,2,3,4-tetrahydro-7-naphthoic acid was dissolved in a solution of 1.5 g. of potassium hydroxide in 5 cc. of water and methylated with 2 cc. of dimethyl sulfate. After heating on the steam-bath for fifteen minutes, the methyl 6-methoxy-1,2,3,4-tetrahydro-7-naphthoate separated out. It crystallized out of 90% methanol in colorless needles melting at 99–100°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.19; H, 7.28.

6-Methoxy-1,2,3,4-tetrahydro-7-naphthoic Acid.—The above methyl ester was hydrolyzed by refluxing with 2 *N* potassium hydroxide until a homogeneous solution was formed. The 6-methoxy-1,2,3,4-tetrahydro-7-naphthoic acid crystallized from dilute methanol in colorless needles, m. p. 113–114°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.87; H, 6.84. Found: C, 69.91; H, 6.91.

Summary

The structures of isomeric *o*-hydroxyaldehydes produced from β -tetralol by the Reimer–Tiemann reaction have been determined.

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