indirect method for determining disulfides. It may be possible to use a procedure similar to an active-hydrogen determination,[8] wherein the disulfide would be estimated from the volume of hydrogen liberated on reaction with excess lithium aluminum hydride. This application is being investigated.

Summary

Lithium aluminum hydride in an ether-type solvent is an effective reducing agent for the disulfide linkage in organic molecules. The reduction involves scission of the sulfur-sulfur bond to form a lithium-aluminum complex and to liberate stoichiometrically the hydrogen of the hydride. Mercaptans are obtained by hydrolysis of the complex with dilute acid.

Tertiary alkyl groups attached to the sulfur-sulfur bond slow the reaction rate, but quantitative reduction may be obtained by using higher temperatures and longer reaction times.

Measurement of liberated hydrogen in lithium aluminum hydride reductions provides the basis for a possible quantitative method for the determination of disulfides.

WHITING, IND. RECEIVED JULY 11, 1949

---

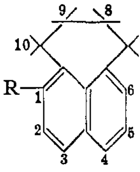
[8] Krynitsky, Johnson and Carhart, THIS JOURNAL, **70**, 486 (1948).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

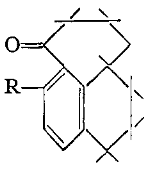
The Synthesis of 1-Hydroxycyclohepta[de]naphthalene[1]

BY RICHARD C. GILMORE, JR., AND W. J. HORTON

The cyclohepta[de]naphthalene ring system, I, has not as yet been reported although a few related compounds are known. von Braun[2] submitted γ-1-tetrylbutyric acid to cyclization and obtained III in low yield. The cyclization of γ-5-methoxy-1-naphthylbutyric acid[3] is almost exclusively toward the peri position. Using phthalic anhydride or succinic anhydride,[4,5] seven-membered ring systems of this type were encountered.

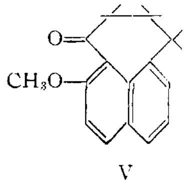


I, R = H
II, R = OH

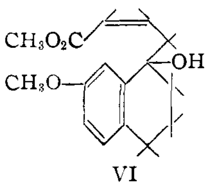


III, R = H
IV, R = OCH_3

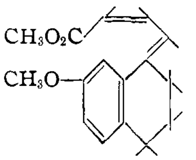
The internal Friedel–Crafts reaction on γ-7-methoxy-1-naphthylbutyryl chloride using stannic chloride gave two different ketones, one of which was converted to a phenanthrene derivative.[6] A keto-cyclohepta[de]naphthalene structure, V, was proposed to account for the second compound.



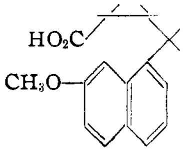
V



VI



VII



VIII

This reaction has been repeated and the peri-cyclized compound, obtained in 19% yield, has been converted, by reduction of the keto group and demethylation, to 1-hydroxycyclohepta[de]-naphthalene, II. In two other independent syntheses of II, compounds were obtained which proved to be identical to the above.

To obtain VIII for the original cyclization, 7-methoxy-1-tetralone[6] and methyl γ-bromocrotonate[7] were treated with zinc and iodine to yield VI. This Reformatsky product was dehydrated to what was assumed to be VII, analogous to a similar case.[8] Reduction, followed by dehydrogenation and saponification, gave VIII, identical to that previously reported.[6]

The reaction of the acid chloride of γ-7-methoxy-1,2,3,4-tetrahydro-1-naphthylbutyric acid for three minutes produced IV in 90% yield.[9] Reduction of the keto group of IV followed by dehydrogenation and demethylation gave II.

A second series of reactions starting with β-methyl naphthyl ether and succinic anhydride gave isomeric β-2-methoxynaphthoylpropionic acids.[10] An improved separation of these isomers gave IX in 25% yield. Reduction of the keto group and cyclization to the 8-position gave

---

[1] From the Doctoral Dissertation of Richard C. Gilmore, Jr.

[2] von Braun and Rath, *Ber.*, **60**, 1182 (1927).

[3] Kon and Soper, *J. Chem. Soc.*, 790 (1939).

[4] Fieser and Peters, THIS JOURNAL, **54**, 4347 (1932); Fieser and Fieser, *ibid.*, **55**, 3010 (1933).

[5] Rieche and Frühwald, *Ber.*, **64**, 1603 (1931).

[6] Bachmann and Horton, THIS JOURNAL, **69**, 58 (1947).

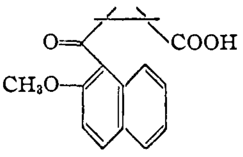
[7] Ziegler, Späth, Schaaf, Schumann and Winkelmann, *Ann.*, **551**, 80 (1942).

[8] Stork, THIS JOURNAL, **69**, 2936 (1947).

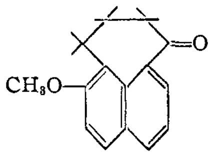
[9] This is in contrast to von Braun's cyclization[2] using aluminum chloride to produce III in 12% yield. The activating effect of a methoxy group has been noted above.[3]

[10] Short, Stromberg and Wiles, *J. Chem. Soc.*, 319 (1936).

X. A Clemmensen reduction of X followed by demethylation gave II.



IX



X

When VI was dehydrated, a crystalline material, VII, was obtained. In one experiment, an appreciable amount of lower boiling liquid was noted. This gave VIII on dehydrogenation and saponification. That this fraction was doubly unsaturated was demonstrated by the fact that it consumed two moles of hydrogen per mole of compound over platinum oxide. The liquid is therefore either a geometrical or a position isomer of the higher boiling crystalline fraction.

When crystalline VII was treated with hydrogen and Raney nickel, one double bond only was attacked since saponification of the product gave a crystalline unsaturated acid in excellent yield.[11]

We wish to express our deep appreciation of a Frederick Gardner Cottrell grant which greatly assisted in this work.

Experimental[12]

Methyl γ-7-Methoxy-1,2,3,4-tetrahydro-1-naphthylidenecrotonate (VII).—A solution of 12.8 g. of 7-methoxy-1-tetralone[6] and 12.5 g. of methyl γ-bromocrotonate[7] in 100 cc. of a solution of equal volumes of anhydrous ether and benzene, was treated with 14.5 g. of 30-mesh zinc and 100 mg. of iodine. Analogous to the reported procedure,[13] three additions of 4.4 g. of bromocrotonic ester, 10 g. of zinc and a crystal of iodine were added hourly for three hours while refluxing in a bath at 60°. A solid complex appeared at once when the iodine was added. After a total time of seven hours, the complex was decomposed in the usual manner.[13] By distillation of the product VI, the usual run produced several grams of forerun and a fraction, 11.1 g. (59%), b. p. 192–195° (0.6 mm.) which crystallized in flat rods from petroleum ether (90–120°), m. p. 90.5–91°.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.37; H, 7.10.

On one of the runs, the lower distilling fraction amounted to 9.0 g., b. p. 160° (0.6 mm.), and the second fraction, 6.8 g., distilled and solidified as before; total yield, 85%. That this forerun was an isomer of the crystalline product was demonstrated by (a) heating with palladium-charcoal[14] at 270–280° for two hours followed by saponification. The product, from methanol, melted at 105–106° and did not depress the m. p. of known γ-7-methoxy-1-naphthylbutyric acid, VIII. (b) Over platinum oxide, two moles of hydrogen were taken up. Saponification of the hydrogenated material gave an acid which did not depress the m. p. of known[6] γ-7-methoxy-1,2,3,4-tetrahydro-1-naphthylbutyric acid.

Attempted dehydration of the product of the Reformatsky reaction by means of phosphorus pentoxide in anhydrous benzene gave mostly polymer. When the supposed carbinol ester VI was dehydrated by heating with potassium acid sulfate for one hour at 160° before distillation, low yields were obtained.

γ-7-Methoxy-1,2,3,4-tetrahydro-1-naphthylidenecrotonic Acid.—A solution of 500 mg. of the crystalline ester, m. p. 90.5–91°, in 1:1 aqueous alcohol containing 3 g. of potassium hydroxide was refluxed for four hours to yield, on acidification, 450 mg. (95%) of acid. Recrystallization from carbon tetrachloride gave colorless rods, m. p. 171–172°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.74; H, 6.61. Found: C, 73.61; H, 6.71.

γ-7-Methoxy-1,2,3,4-tetrahydro-1-naphthylidenebutyric Acid.—A solution containing 2.0 g. of distilled Reformatsky ester VII, m. p. 90.5–91°, in 50 cc. of absolute ethanol consumed one mole of hydrogen per mole of ester when shaken with 1.0 g. of Raney nickel at a pressure of 30 pounds. Filtration and evaporation of the solvent gave the ester which could not be crystallized. Saponification by refluxing in 50 cc. of 1:1 aqueous ethanol containing 3 g. of potassium hydroxide for five hours gave, after crystallization from petroleum ether (60–90°), 1.85 g. (97%) of acid; long flat plates, m. p. 98.5–99°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.36. Found: C, 73.54; H, 7.21.

γ-7-Methoxy-1,2,3,4-tetrahydro-1-naphthylbutyric Acid.—A solution containing 1.29 g. of the same ester in absolute alcohol, consumed two moles of hydrogen per mole of compound when shaken over platinum oxide at a pressure slightly above atmospheric. Since the product could not be crystallized, it was refluxed with 1.2 g. of potassium hydroxide in 100 cc. of 1:1 aqueous ethanol. Acidification produced acid which distilled at 165° (1.0 mm.) and crystallized when cooled and rubbed with petroleum ether (60–90°). Recrystallization gave 1.2 g., m. p. 59–61° (reported[6] 59.5–62°).

1-Methoxy-10-ketocyclohepta[de]naphthalene.—The cyclization of 5.0 g. of VIII (prepared from the tetrahydro-compound as reported[6]) by means of stannic chloride following the published procedure[6] closely, gave a 97% yield of mixed ketones from which 1-keto-6-methoxy-1,2,3,4-tetrahydrophenanthrene, m. p. 100–102°, was separated by crystallization from aqueous methanol. Addition of an equal volume of water to the mother liquor and three hours of standing gave 0.86 g. (19%) of long prisms, m. p. 81–82.5°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.63; H, 6.24. Found: C, 79.55; H, 6.04.

When phosphorus pentachloride was used rather than thionyl chloride for the preparation of the acid chloride, no material melting at the lower temperature could be found.

1-Hydroxycyclohepta[de]naphthalene (II).—Reduction of 0.25 g. of the above ketone, m. p. 81–82.5°, by means of the usual Clemmensen procedure[15] gave 0.20 g. (85%) of oil which could not be crystallized. When this was refluxed with a solution of 10 cc. of 48% hydrobromic acid and 20 cc. of glacial acetic acid for twenty-four hours, the product, after vacuum distillation of the solvent, dissolved in 20 cc. of 5% aqueous sodium hydroxide. On addition of dilute hydrochloric acid and cooling in an ice-chest overnight, long colorless needles appeared. These were mechanically removed from the brown material present and purified by crystallization from petroleum ether (30–60°). Long rods were obtained, m. p. 82–83.5°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 85.08; H, 7.10.

1-Methoxy-10-keto-4,5,6,6a-tetrahydrocyclohepta[de]-naphthalene (IV).—A solution of 5.0 g. of γ-7-methoxy-1,2,3,4-tetrahydro-1-naphthylbutyric acid in 150 cc. of anhydrous benzene was cooled to the point of crystallization. Five grams of phosphorus pentachloride was added and the mixture allowed to stand at room temperature overnight. The solution was cooled in ice-water, 5.5 cc. of anhydrous stannic chloride was added with swirling

---

[11] *Cf.* ref. 8 for a similar case.

[12] Melting points are uncorrected.

[13] Bachmann and Wendler, THIS JOURNAL, **68**, 2580 (1946).

[14] Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

[15] Martin, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 155.

and the reaction allowed to continue for three minutes. The mixture was poured into a 1:1 solution of ether and concentrated hydrochloric acid containing ice. The layers obtained were separated and the aqueous solution was extracted twice with ether. The combined ether solutions, after washing twice with 1:1 hydrochloric acid, water, twice with 10% aqueous sodium hydroxide and then water, was dried and concentrated. The residual oil weighed 4.5 g. (90%) and boiled at 167–170° (1.0 mm.).

A mixture containing 1.0 g. of distilled oil, 1.8 g. of semicarbazide hydrochloride, 0.75 cc. of pyridine and 45 cc. of absolute alcohol was refluxed for seventeen hours. After distillation of the alcohol, the residue was washed twice with water by decantation. The residue, moistened with petroleum ether (30–60°), solidified and was recrystallized from *o*-xylene, giving 1 g. of colorless rods, m. p. 192.5–193.5°.

Anal. Calcd. for $C_{16}H_{21}O_2N_3$: N, 14.7. Found: N, 15.09.

1-Methoxy-4,5,6,6a-tetrahydrocyclohepta[de]naphthalene.—Reduction of 3.0 g. of the above ketone using 20 g. of amalgamated zinc and toluene and the usual procedure[15] gave a product distilling at 130° (1.0 mm.). The distillate crystallized and was further purified from aqueous acetic acid to yield 2.5 g. of long colorless needles (89%), m. p. 46–47°.

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.30. Found: C, 83.12; H, 9.01.

1-Hydroxycyclohepta[de]naphthalene (II) (from the methoxytetrahydro derivative).—When 1.5 g. of the above tetrahydro derivative was heated with 0.15 g. of palladium-charcoal[14] for two hours at 270–280°, hydrogen was evolved. Approximately two moles per mole of compound was obtained. The residue, 1.3 g. (98%), was refluxed with hydrobromic-acetic acid mixture as previously described. Material, soluble in aqueous sodium hydroxide, distilled at 140–145° (0.25 mm.) and crystallized when rubbed with petroleum ether (30–60°), m. p. 75.5–78°, yield, 20 mg. (4%). Purification from petroleum ether gave material melting 82–83.5°, unchanged when mixed with the previously obtained material.

β-2-Methoxy-1-naphthoylpropionic Acid[10] (IX).—A solution of 106 g. of anhydrous aluminum chloride in 440 cc. of nitrobenzene was prepared by warming gently. The solution was cooled, 42 g. of succinic anhydride was added and the mixture cooled with mechanical stirring to −12 to −16°. Over a period of one hour, 65 g. of 2-methoxynaphthalene, m. p. 72–73.5°, was added and the mixture was held at this temperature with stirring for two hours. It was then allowed to come to room temperature and stand overnight. Decomposition by ice and hydrochloric acid followed by steam distillation of the nitrobenzene gave a sticky cake which, after discarding the supernatant liquid, was dissolved in aqueous sodium bicarbonate by warming for six hours. By filtering while warm, cooling and acidification, 74 g. of a dry crude acid mixture, m. p. 118–122°, was obtained. The acid mixture was esterified by refluxing with 500 cc. of 6.5% ethanolic hydrogen chloride for twenty-four hours. Evaporation of the solvent and vacuum distillation gave 26.5 g. (25%) of the ethyl ester of IX, b. p. 199–204° (0.7 mm.), m. p. 40–42° (reported[10] 41–42°). The ethyl ester of the 6-isomer was available in the residue. Saponification of the ester of the 1-isomer gave IX in quantitative yield, m. p. 135.5–136° (reported[10] 136.5–137.5°).

γ-2-Methoxy-1-naphthylbutyric Acid.—Reduction of 23.5 g. of IX with 50 g. of amalgamated zinc in the usual way[15] gave the butyric acid in quantitative yield. Recrystallized from petroleum ether (60–90°), colorless diamond-shaped plates were obtained which melted at 88.5–90°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.74; H, 6.61. Found: C, 73.95; H, 6.61.

1-Methoxy-7-ketocyclohepta[de]naphthalene (X).—A solution of 3.5 g. of the above acid in 100 cc. of anhydrous benzene was converted to the acid chloride by addition of 3.12 g. of phosphorus pentachloride to the cold benzene solution and standing at room temperature overnight. Addition of 4.5 cc. of anhydrous stannic chloride gave a dark red insoluble complex within fifteen minutes. The mixture was decomposed and treated as in the previous cyclization. The product (3.0 g., 94%) crystallized from petroleum ether (60–90°) in long colorless hexagonal prisms, m. p. 66–67.5°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.63; H, 6.24. Found: C, 79.92; H, 6.20.

1-Hydroxycyclohepta[de]naphthalene (II) (from X).—The Clemmensen reduction of 1 g. produced an oil. When 0.8 g. of the oil was demethylated as before, colorless needles were isolated. From petroleum ether (30–60°), 5 mg. was obtained, m. p. 82–83.5°, not changed by admixture with the compounds obtained previously. When the demethylation procedure was conducted under nitrogen, no decrease in the loss by decomposition could be noted.

Summary

Two syntheses designed to give 1-hydroxycyclohepta[de]naphthalene resulted in identical compounds. By conversion of the unknown ketone from the cyclization of γ-7-methoxy-1-naphthylbutyryl chloride to the above cyclohepta[de]naphthalene, its structure has been conclusively demonstrated.

SALT LAKE CITY, UTAH

RECEIVED JULY 19, 1949