homolog of Tryparsamide) was prepared from its ethyl ester.[5]

Experimental

Preparation of I and II.—These compounds were prepared by the method given for N-4-arsonophenylglycine.[3] One variation in purification that was found necessary to remove final traces of unreacted bromopropionic acids was washing the products several times with ether; yields I (65%), II (41%).

Anal. Calcd. for $C_9H_{12}AsNO_5$: As, 25.99. Found: (I) As, 25.50; (II) As, 25.91.

Preparation of III and IV.—These compounds were prepared by the method given for 4-arsonophenoxyacetic acid[4]; yields III (37%), IV (5%).

Anal. Calcd. for $C_9H_{11}AsO_6$: As, 25.86. Found: (III) As, 25.90; (IV) As, 25.80.

Preparation of Ethyl Esters of I, II and III.—Prepared by the method used for the esterification of N-4-arsonophenylglycine[5]; yields I (45%), II (60%), III (50%).

Anal. Calcd. for $C_{11}H_{16}AsNO_5$: As, 23.69. Found: (I) As, 23.30; (II) As, 23.60. Calcd. for $C_{11}H_{15}AsO_6$: As, 23.63. Found: (III) As, 23.50.

Preparation of the Amide of I.—Prepared by ammonolysis of the ethyl ester using the method given for the amide of N-4-arsonophenylglycine[5]; yield 52%.

Anal. Calcd. for $C_9H_{13}AsN_2O_4$: As, 26.04; N, 9.72. Found: As, 26.0; N, 9.15.

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Preparation of 3-(6-Methoxynaphthyl-2)-2-cyclohexen-1-one and Related Compounds

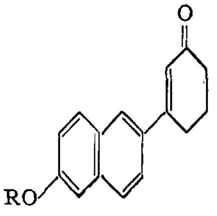
BY FREDERICK C. NOVELLO AND MARCIA E. CHRISTY

RECEIVED JULY 14, 1953

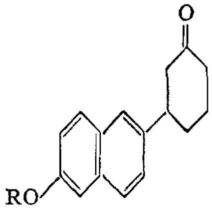
The condensation reaction between aryl β-dialkylamino ketones and acetoacetic ester and related compounds containing an active methylene group offers a convenient method for preparing 3-aryl-2-cyclohexen-1-one derivatives.[1] This procedure was employed to prepare 3-(6-methoxynaphthyl-2)-2-cyclohexen-1-one (I) and the related compounds, II–VII, which were of interest in view of the estrogenic activity of 1-ethyl-2-(4-hydroxyphenyl)-6-hydroxy-1,2,3,4-tetrahydronaphthalene and 1-methyl-2-(4-hydroxyphenyl)-6-methoxy-3,4-dihydronaphthalene.[2]

Synthesis of I was accomplished by condensation between 2-(β-dimethylaminopropionyl)-6-methoxynaphthalene hydrochloride and acetoacetic ester in the presence of alcoholic potassium hydroxide. Demethylation to II was effected by brief treatment with aluminum chloride in boiling xylene.[3] Conversion of I and II to the cyclohexanone and cyclohexanol derivatives, III–VII, was carried out by catalytic hydrogenations. Separation of stereoisomers was not attempted although V and VI were isolated as apparent homogeneous crystalline entities; VII was obtained as a glass. In the course of these hydrogenation studies it was found that vigorous stirring was superior to conventional methods of agitation and in the reduction of 3-(6-methoxynaphthyl-2)-2-cyclohexen-1-one to the cyclohexanone III, a sixfold increase in the reaction rate was realized when vigorous stirring was employed.

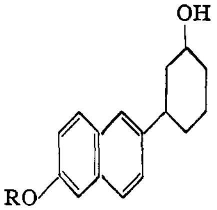
Of this series, 3-(6-hydroxynaphthyl-2)-2-cyclohexen-1-one (II) was the most active and gave a positive estrogenic response at a dosage level of 500 μg. in the vaginal cornification assay procedure.[4]



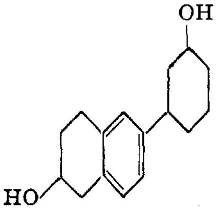
I, R = CH_3
II, R = H



III, R = CH_3
IV, R = H



V, R = CH_3
VI, R = H



VII

Experimental[5]

2-(β-Dimethylaminopropionyl)-6-methoxynaphthalene Hydrochloride.—A mixture of 37.5 g. (0.19 mole) of 2-acetyl-6-methoxynaphthalene,[6] 16.3 g. of dimethylamine hydrochloride, 8.8 g. of paraformaldehyde in 100 ml. of ethanol and 5 drops of concentrated hydrochloric acid was refluxed for 48 hours and concentrated to dryness *in vacuo*. The residual solid was suspended in ether, collected on a funnel and crystallized from ethanol; yield 39.1 g. (70%) of yellow needles, m.p. 180–184°. After further recrystallizations, pale yellow needles were obtained, m.p. 184–185.5°.

Anal. Calcd. for $C_{16}H_{20}O_2NCl$: C, 65.41; H, 6.86; N, 4.77. Found: C, 65.21; H, 7.04; N, 4.73.

The free base was obtained as colorless plates, m.p. 77–79°, from ether–petroleum ether.

Anal. Calcd. for $C_{16}H_{19}O_2N$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.47; H, 7.41; N, 5.41.

3-(6-Methoxynaphthyl-2)-2-cyclohexen-1-one (I).—A solution of 11.5 g. of potassium hydroxide in 150 ml. of isopropyl alcohol was added to a well-stirred mixture of 30 g. (0.1 mole) of 2-(β-dimethylaminopropionyl)-6-methoxynaphthalene hydrochloride and 13.1 g. of methyl acetoacetate in 150 ml. of isopropyl alcohol. The mixture was heated to reflux and stirred until the mixture became too viscous to allow further stirring (4–5 hours). After heating for a total of 72 hours, the mixture was poured into 3 l. of water and allowed to cool. The product was collected on a funnel, sucked dry, and then digested on the steam-bath with 200 ml. of benzene. The filtered benzene solution was washed with 10% hydrochloric acid, water and dried over sodium sulfate. After removal of solvent, the residue was distilled at 0.5 mm. and the product crystallized from acetone; yield 18.0 g. (70%) of yellow needles, m.p. 138–141°. An analytical sample was obtained by repeated recrystallizations from acetone as pale yellow needles, m.p. 142.3–143.3°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; OCH_3, 12.30. Found: C, 81.00; H, 6.45; OCH_3, 12.24.

The oxime derivative crystallized from alcohol as pale yellow plates, m.p. 171.2–172.5°.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.41. Found: C, 76.40; H, 6.45.

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[4] The authors are indebted to Dr. Roland K. Meyer and Dr. Elva S. Meyer, University of Wisconsin, for the estrogenic assays.

[5] The authors are indebted to Mr. Kermit B. Streeter and his associates, Miss J. L. Pyett and Mr. J. P. Laux for the analytical data.

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3-(6-Hydroxynaphthyl-2)-2-cyclohexen-1-one (II).—A solution of 2 g. of I in 20 ml. of xylene was refluxed with 4.0 g. of aluminum chloride for 5 minutes and poured onto ice and dilute hydrochloric acid. The solid was collected on the filter and taken up in acetone–benzene. The organic extract was washed with water and then extracted with 5% sodium hydroxide. The alkaline solution was acidified and the product collected on the filter and purified through its sparingly water-soluble sodium salt; yield 1.2 g. (63.5%) tan plates, m.p. 210–212°. Repeated crystallizations from alcohol gave pale yellow plates, m.p. 215.1–217.4°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.70; H, 5.95.

An oxime was obtained as pale yellow needles from alcohol-hexane, m.p. 234.7–238.4°.

Anal. Calcd. for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97. Found: C, 75.75; H, 6.12.

3-(6-Methoxynaphthyl-2)-cyclohexanone (III).—A solution of 30 g. (0.12 mole) of 3-(6-methoxynaphthyl-2)-2-cyclohexen-1-one in 160 ml. of purified dioxane[7] was hydrogenated at atmospheric pressure in the presence of 7.0 g. of 5% palladium-on-charcoal catalyst[8] with vigorous stirring[9] at 55°. Reduction ceased upon saturation of the ethylenic double bond. After removal of catalyst and solvent, the product was crystallized from ethanol; yield 18.4 g. (60%) of colorless needles, m.p. 116–119°. Further recrystallizations from ethanol afforded a sample melting at 124–125°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13; OCH_3, 12.20. Found: C, 80.29; H, 7.05; OCH_3, 12.28.

An oxime was obtained as colorless needles from alcohol, m.p. 152.5–154°.

Anal. Calcd. for $C_{17}H_{19}O_2N$: C, 75.80; H, 7.11. Found: C, 75.53; H, 7.12.

3-(6-Methoxynaphthyl-2)-cyclohexanol (V).—A solution of 1 g. of 3-(6-methoxynaphthyl-2)-2-cyclohexen-1-one in 50 ml. of ethanol was hydrogenated in the presence of 150 mg. of platinum catalyst until hydrogen absorption ceased (24 minutes). The product crystallized from alcohol–hexane as colorless needles; yield 0.55 g., m.p. 122–124°. Further recrystallizations from alcohol–water gave colorless plates, m.p. 127.6–129.2°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.87. Found: C, 79.72; H, 8.02.

3-(6-Hydroxynaphthyl-2)-cyclohexanone (IV).—A solution of 0.5 g. of 3-(6-hydroxynaphthyl-2)-2-cyclohexen-1-one in 35 ml. of glacial acetic acid was hydrogenated in the presence of 100 mg. of palladium black catalyst until reduction ceased (50 minutes). After removal of catalyst and solvent, the residue was distilled at 0.3 mm. and the distillate crystallized from benzene–hexane; yield 200 mg. of pale yellow needles, m.p. 142.6–145.3°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.89; H, 6.81.

3-(6-Hydroxynaphthyl-2)-cyclohexanol (VI).—A solution of 1 g. of 3-(6-hydroxynaphthyl-2)-2-cyclohexen-1-one in 100 ml. of ethanol was hydrogenated in the presence of 1 g. of WF-7 nickel catalyst[10] at atmospheric pressure until reduction ceased. After removal of catalyst and solvent, the residue was taken up in ether, washed with water and dried. The product was obtained from acetone–petroleum ether as pale yellow plates; yield 250 mg., m.p. 183–194°. Further recrystallizations from alcohol–water afforded colorless needles, m.p. 217.1–218.4°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.45; H, 7.56.

2-Hydroxy-6-(3-hydroxycyclohexyl)-tetralin (VII).—A solution of 2 g. of 3-(6-hydroxynaphthyl-2)-2-cyclohexen-1-one in 50 ml. of alcohol containing 20 mg. of sodium hydroxide was hydrogenated in a bomb in the presence of 600 mg. of Raney nickel catalyst at 130° for 12 hours. The colorless alcoholic solution was filtered and concentrated on the steam-bath. The concentrate was taken up in ether and washed with dilute sodium hydroxide, water and dried over sodium sulfate. The product was obtained by distillation at 0.5 mm. as a colorless glass; yield 1.6 g.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.95; H, 9.14.

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WEST POINT, PENNA.

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[7] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Edition, D. C. Heath and Company, Boston, Mass., 1941, p. 368.

[8] Baker and Co., Inc., Catalysts, Newark, N. J.

[9] A 3-necked round bottom flask served as the reaction vessel and stirring was accomplished with a stainless steel stirrer made gas tight by means of a stainless steel stuffing box and driven by a 1/2 h.p. drill press at 1750 r.p.m.

[10] H. R. Billica and H. Adkins, *Org. Syntheses*, **29**, 24 (1949).

Studies in Low Concentration Chemistry. V. The Spontaneous Deposition of Silver-111 on Various Metals

BY GEORGE K. SCHWEITZER AND DALE L. WILHELM

RECEIVED JULY 2, 1953

In the past fifty years, numerous publications have indicated an interest in the spontaneous deposition of carrier-free radionuclides from solution onto metal foils. A detailed bibliography of these researches has been compiled by Bonner.[1] Most of the investigators assumed that the process involved was a simple electrochemical displacement. If one makes this assumption, a knowledge of the critical deposition potential of the carrier-free nuclide should allow a prediction to be made as to which solution–metal foil conditions would bring about deposition of the tracer. Such a deposition potential for silver-111 has been measured and a value of −0.77 v. is reported.[2] In most previous experiments, no metal salts of the metal foils were added to the solutions, making it difficult to assign a metal foil potential, and to predict deposition behavior. Erbacher,[3] Joliot[4] and Camarcat, Bouissieres and Haissinsky[5] have helped to clarify the situation by measuring the potentials of various metal foils in solutions to which no corresponding metal salts had been added. However, several depositions have been reported which should not occur according to the relationship of these so-called "anomalous metal potentials" to the deposition potentials of the ions.[1]

This research was undertaken in order to investigate the spontaneous deposition of carrier-free silver-111 onto various metal foils in the absence of ions of the metal.

Experimental

Materials.—The silver-111 isotope was produced by neutron irradiation of palladium foil at the Oak Ridge National Laboratory. Perchloric acid solutions of this radionuclide were prepared by the procedure of Schweitzer and Nehls.[6] Spectrographic analysis of the palladium foil indicated that the silver solutions had a concentration of about 10^{-8} *M*. All inactive chemicals used in these experiments were reagent grade and all solutions were prepared using distilled water. All metal foils were cut square 2.0 cm. on an edge with a short strip 0.3 cm. wide appended by which they could be attached to a support. The foil thicknesses ranged

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[1] A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 169–171, 450–459.

[2] L. Rogers, D. Krause, J. Greiss and D. Ehrlinger, *J. Electrochem. Soc.*, **95**, No. 2, 33 (1949).

[3] O. Erbacher, *Z. physik. Chem.*, **156A**, 135 (1931).

[4] F. Joliot, *J. chim. phys.*, **27**, 119 (1930).

[5] M. Camarcat, G. Bouissieres and M. Haissinsky, *ibid.*, **46**, 153 (1949).

[6] G. K. Schweitzer and J. W. Nehls, THIS JOURNAL, **74**, 6186 (1952).