Experimental

Tetrahydrofurfuryl Mesylate.—To a cooled solution of 51 g. (0.5 mole) of tetrahydrofurfuryl alcohol in 50 cc. of pyridine was added dropwise, with shaking, a mixture of 63 g. (0.55 mole) of mesyl chloride and 20 cc. of pyridine. After the reaction mixture had been allowed to stand in a refrigerator overnight, chopped ice and sufficient water to dissolve the pyridine hydrochloride were added. The product was extracted with four 40-cc. portions of chloroform. The chloroform extracts were combined and dried over anhydrous sodium sulfate. After removal of the chloroform, 64.2 g. (71%) of a product was obtained which boiled at 102–105° (2 mm.); $n^{20}D$ 1.4625.

Anal. Calcd. for $C_6H_{12}O_4S$: C, 40; H, 6.73; S, 17.8. Found: C, 39.7, 40.0; H, 6.96, 7.17; S, 17.7, 18.0.

Tetrahydrofurylacetonitrile.—Nine grams (0.05 mole) of the mesyl ester and 6.5 g. (0.1 mole) of potassium cyanide were placed in a 50-cc. round-bottomed flask and allowed to react on a steam-bath for four days. The contents of the flask were extracted with three 15-cc. portions of ether. The ether extracts were combined, dried and concentrated. Two grams of a colorless product, boiling at 45° (2 mm.), was collected; $n^{15}D$ 1.4490, 36% yield.[4]

***s*-Butyl Mesylate and Potassium Cyanide.**—*s*-Butyl mesylate (15 g.) and potassium cyanide (10 g.) were heated at 100° in a flask connected to a gas washing bottle containing 8 cc. of liquid bromine in 200 cc. of carbon tetrachloride. After twenty-four hours the excess bromine was removed by treatment with sodium bisulfite. The mixture was washed with three 25-cc. portions of water, the carbon tetrachloride layer was dried over anhydrous sodium sulfate and concentrated at reduced pressure. A colorless liquid (8.1 g.), boiling at 160–161°, was obtained; yield of 2,3-dibromobutane was 38%.

Anal. Calcd. for $C_4H_8Br_2$: Br, 74.0. Found: Br, 73.8, 73.9.

---

[4] Barger, Robinson and Smith, *J. Chem. Soc.*, 718 (1937).

SUGAR RESEARCH FOUNDATION LABORATORY
DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

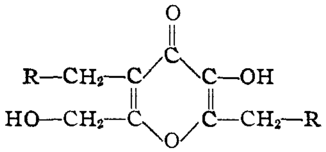
RECEIVED SEPTEMBER 3, 1946

Mannich Bases from Kojic Acid and Aryl Amines

BY L. L. WOODS

Experiments have shown that kojic acid reacts with aryl amines and formalin to produce Mannich bases. Analysis of the resulting bases indicates that the reaction takes place not only at position 3, as expected, but at some other position also.

TABLE I



R	Method	Yield, g.	M. p.,[b] °C.	Formula	% Nitrogen[c] Calcd.	% Nitrogen[c] Found
Anilino	A	5.2	263.9 charring	$C_{20}H_{20}N_2O_4$	7.95	7.87
Methylanilino	B	7.0	116–117 dec.	$C_{22}H_{24}N_2O_4$	7.38	7.33
p-Toluino	B[a]	5.1	148.4–148.9 dec.	$C_{22}H_{24}N_2O_4$	7.38	7.66
p-Bromoanilino	B	8.3	185.2 dec.	$C_{20}H_{18}N_2O_4Br_2$	5.49	5.43

[a] Also by method A with poor yields. [b] Corrected, and melted with decomposition. [c] All nitrogen analyses were by the Kjeldahl method.

In considering the view that the hydroxyl at position 5 on kojic acid is phenolic[1,2] and the recent results obtained by Holdren[3] with furans it is not surprising that kojic acid possesses two centers of activity, positions 3 and 6; also, the only places where the reaction could take place without rearrangement. The compounds reported have been named on the assumption that such a structure is correct.

All of the Mannich bases produced by these experiments were crystalline. Three of the bases were light tan in color and soluble in acetone and ether. The aniline derivative which was greenish-yellow exhibited a sparing solubility in these solvents. When the bases were dissolved in dilute hydrochloric acid and a little ferric chloride added, a faint but unmistakable red coloration was obtained.

Procedures

Method A.—To 0.03 mole (4.23 g.) of kojic acid in 50 ml. of methanol about 3 ml. of concentrated hydrochloric acid was added, followed by 1 g. of paraformaldehyde and 0.03 mole of the aryl amine. The solution was then tested with congo red paper and if the solution was not acid sufficient hydrochloric acid was added to give an acid reaction. The resulting mixture was heated under reflux over a boiling water-bath for half an hour, cooled, and then poured into 300 ml. of water. The mixture was next made basic with ammonium hydroxide and allowed to stand over night. Since the precipitated base adhered strongly to glass the supernatant liquid was decanted carefully. Purification of the material was effected by dissolving the base in warm dilute hydrochloric acid and then adding 300 ml. of water. The solution was filtered, made just basic with ammonium hydroxide and allowed to stand until precipitation appeared to be complete. The base was then obtained by filtration. In instances where the product was not crystalline and light tan in color, as in the case of the *p*-bromoaniline and methylaniline derivatives, the material was dissolved in the smallest amount of acetone possible and then precipitated with 300–400 ml. of water. Since this treatment caused the compounds to separate as a very finely divided precipitate it usually required several days standing before filtration. The bases were dried in the vacuum desiccator.

Method B.—To a mixture of 0.03 mole (4.23 g.) of kojic acid, 25 ml. of 37% formalin and about 3 ml. of concentrated hydrochloric acid, 0.03 mole of aryl amine was

---

[1] Tokuro Soda, *et al.*, *J. Chem. Soc. Japan*, **61**, 1227–1232 (1940).

[2] R. Adams, "Organic Reactions," Vol. 1, John Wiley and Sons, New York, N. Y., 1942, p. 311.

[3] Holdren and Hixon, THIS JOURNAL, **68**, 1198 (1946).

added. The mixture was heated for fifteen minutes on a steam-bath and then diluted with 300 ml. of water. The precipitation and purification of the base was as described in method A.

SAINT AUGUSTINE'S COLLEGE
RALEIGH, NORTH CAROLINA
RECEIVED AUGUST 20, 1946

NEW COMPOUNDS

3,4-Dimethoxy-10-methyl-2,4,7-naphthitatrien-1-one[1]

Methylation of the sodium derivative from 1 g. of 2-methoxy-5-methyl-2,7-naphthitadiene-1,4-dione[2] (0.13 g. of sodium in liquid ammonia) in benzene using 2 g. of methyl iodide, which was added in three portions during twenty-six hours, gave 657 mg. of crude crystals. One recrystallization from benzene followed by two from hexane gave nearly colorless needles, m. p. 136–137° (cor.).

Anal.[3] Calcd. for $C_{13}H_{16}O_3$: C, 70.9; H, 7.3. Found: C, 70.5; H, 7.1.

In a second experiment 5 g. of the monomethoxydione gave 4.3 g. of crude dimethyl ether; once crystallized from hexane, it melted at 129–132°. A few mg. on a steam-bath with three drops of concentrated hydrochloric acid for twenty minutes gave 5-methyl-7-naphthitene-1,2,4-trione enol, m. p. 165–169°; mixed with authentic material[4] m. p. 166–170°.

---

[1] This work was supported by an allotment from the Special Research Fund (Bankhead-Jones Act of June 29, 1935). Not subject to copyright.

[2] Orchin and Butz, *J. Org. Chem.*, **8**, 509 (1943).

[3] By Dr. T. S. Ma, University of Chicago.

[4] Butz and Butz, *J. Org. Chem.*, **8**, 497 (1943).

BUREAU OF ANIMAL INDUSTRY
AGRICULTURAL RESEARCH ADMINISTRATION
UNITED STATES DEPARTMENT OF
AGRICULTURE
BELTSVILLE, MARYLAND
BENJAMIN L. DAVIS
LEWIS W. BUTZ
RECEIVED SEPTEMBER 13, 1946

Salicylobutylamide and *o*-Nitroacetophenone 2,4-Dinitrophenylhydrazone[1]

Salicylobutylamide.—Methyl salicylate (108 g.) and *n*-butylamine (60 g.) were refluxed together for seven hours. Volatile material was then expelled up to 160° (30 mm.) and the 125 g. of sirupy residue was distilled at 153–156° at 3 mm. The salicylobutylamide was a colorless, viscous sirup.

Anal. (by R. Pivan) Calcd. for $C_{11}H_{15}NO_2$: N, 7.35. Found: N, 7.43.

***o*-Nitroacetophenone 2,4-Dinitrophenylhydrazone.**—A mixture of 2 g. of 2,4-dinitrophenylhydrazine, 1.5 g. of *o*-nitroacetophenone and 100 ml. of alcohol was heated to boiling, 2 ml. of concd. hydrochloric acid was added, and the mixture was boiled under a reflux condenser for five minutes. Copious separation of crystals occurred on cooling. Recrystallization from alcohol gave a pure product, m. p. 152–154° cor.

Anal. (by W. Brandt) Calcd. for $C_{14}H_{11}O_6N_5$: N, 20.29. Found: N, 20.18.

No success attended efforts to synthesize *o*-nitroacetophenone oxime by direct reaction of the ketone with hydroxylamine, although apparently such a compound can be made[2] by reaction of a nitrite on *o*-nitroethylbenzene.

---

[1] This work was done under contracts, recommended by the National Defense Research Committee and the Committee on Medical Research, between the Office of Scientific Research and Development and Northwestern University.

[2] Hochster Farbw., German Patent 109,663; *Chem. Zentr.*, **71**, II, 458 (1900).

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS
CHARLES D. HURD
OTIS E. FANCHER
WILLIAM A. BONNER
RECEIVED MAY 16, 1946

A New Acetylene Silver Nitrate Complex

The customary precipitate formed by interaction of acetylene with aqueous silver nitrate solutions has been considered to have the formula $Ag_2C_2\cdot AgNO_3$, having a crystal form of fine needles and crosses. We find this conclusion to be true for only dilute solutions. As the silver nitrate concentration of the solution is raised above about 10%, there is a tendency for rhombohedral crystals to form and above about 25% silver nitrate concentration the rhombs form to the exclusion of the needles. We have found these rhombs to have the formula of $Ag_2C_2\cdot 6AgNO_3$.

When 80 ml. of acetylene is bubbled through 25 ml. of 30% aqueous silver nitrate at 25° and atmospheric pressure, the acetylene is at first completely absorbed to form a clear solution, followed toward the end of the absorption by the appearance of the white rhombohedral crystals. The mixture is then filtered by suction through a fritted glass filter, washed with acetone and dried at first by suction and then in a vacuum desiccator over sulfuric acid. These rhombs were analyzed by us for silver carbide and total silver gravimetrically and for water-soluble silver volumetrically. We previously found that an acidimetric titration of the filtrate from the rhombs showed free acid equivalent to that customarily released by the acetylene present.

Anal. Calcd. for $Ag_2C_2\cdot 6AgNO_3$: Ag_2C_2, 19.19; $AgNO_3$, 80.81. Found: Ag_2C_2, 19.13; $AgNO_3$, 81.30 (molar ratio 1 to 5.97).

This substance crystallizes in the rhombohedral system; it has a characteristic X-ray diffraction pattern, differing from that of $AgNO_3$ or $Ag_2C_2\cdot AgNO_3$. It has a great tendency to form supersaturated solutions. Upon heating, it first melts and then suddenly but feebly decomposes with the evolution of red vapors of nitrogen oxides above 308° and below 327°, the respective melting points of sodium nitrate and metallic lead. This datum is to be contrasted with a detonating point of about 212° which we have found for $Ag_2C_2\cdot AgNO_3$.

Water decomposes the rhombs to $Ag_2C_2\cdot AgNO_3$ and silver nitrate. Likewise, any reagent that acts to reduce the silver nitrate concentration of the solution in which the rhombs may be existing tends to destroy them in favor of the precipitation of $Ag_2C_2\cdot AgNO_3$. An excess of acetylene added to the solution will act in this manner, as acetylene removes about fifty times its own weight of silver nitrate from solution under these conditions. Conversely, if rhombs and needles exist in the same solution the needles can be completely removed by increasing the silver nitrate concentration, the normal silver carbide being very soluble in strong silver nitrate.

Contribution from the Multiple Fellowship on Gas Purification sustained by Koppers Company, Inc., Pittsburgh, Penna.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PA.
JOSEPH A. SHAW
ELTON FISHER
RECEIVED AUGUST 9, 1946