TABLE I

MELTING POINTS, YIELDS AND ANALYSES

Compound	M. p., °C.	Yield, %	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
2-Methylindanedione	83–85[a]	31	$C_{10}H_8O_2$				
2-Ethylindanedione	53–55[b]	32	$C_{11}H_{10}O_2$				
2-*n*-Propylindanedione	48–49.5[c]	17	$C_{12}H_{12}O_2$				
2-*n*-Butylindanedione	35[d,e]	18	$C_{13}H_{14}O_2$				
Ethyl 2-methylindanedionyl-2-acetate	91–92[f]	62	$C_{14}H_{14}O_4$	68.3	5.7	68.5	6.0
Ethyl 2-ethylindanedionyl-2-acetate	77–78.5	68	$C_{15}H_{16}O_4$	69.2	6.2	69.3	6.3
Ethyl 2-*n*-propylindanedionyl-2-acetate	Oil	[g]	$C_{10}H_{18}O_4$				
Ethyl 2-*n*-butylindanedionyl-2-acetate	Oil	[g]	$C_{17}H_{20}O_4$				
2-Methyl-3-carbethoxynaphthohydroquinone	100–101	44	$C_{14}H_{14}O_4$	68.3	5.7	68.3	5.7
2-Ethyl-3-carbethoxynaphthohydroquinone	110.5–111	68	$C_{15}H_{16}O_4$	69.2	6.2	69.5	6.2
2-*n*-Propyl-3-carbethoxynaphthohydroquinone	125–126.5	14[h]	$C_{16}H_{18}O_4$	70.0	6.6	69.9	6.8
2-*n*-Butyl-3-carbethoxynaphthohydroquinone	98.5–100	24[h]	$C_{17}H_{20}O_4$	70.8	7.0	70.7	7.1
2-Methyl-3-carbethoxynaphthoquinone	99–100	92	$C_{14}H_{12}O_4$	68.8	5.0	69.0	5.2
2-Ethyl-3-carbethoxynaphthoquinone	47.5–48	88	$C_{15}H_{14}O_4$	69.7	5.5	69.6	5.3
2-Ethyl-3-hydroxynaphthoquinone	137.5–138.5[i]	36	$C_{13}H_{10}O_3$	71.3	5.0	71.5	5.4
2-*n*-Butyl-3-hydroxynaphthoquinone	100–101[j]	55	$C_{14}H_{14}O_3$				

[a] Reported [Wojack, *Ber.*, **71**, 1102 (1938)] m. p. 84–85°. [b] Reported (ref. *a*) m. p. 55.5°. [c] Reported (ref. *a*) m. p. 50.5°. [d] B. p. 155–160° at 1 mm. [e] Reported (ref. *a*) m. p. 33°. [f] Reported[4] m. p. 161–162°. Possibly Gheorgiu had a hydrolysis product rather than ester. [g] Not purified. [h] Over-all, including preceding step. [i] Reported [Hooker, THIS JOURNAL, **58**, 1178 (1936)] m. p. 138.2–138.5°. [j] Reported [Hooker, *ibid.*, **58**, 1167 (1936)] m. p. 101–101.5°.

gave a solid which was removed, dissolved in acetic acid (10 ml.) and treated with a solution of chromic acid (0.5 g.) in water. This mixture was heated on a water-bath for fifteen minutes and then diluted with water. The resulting precipitate was obtained in the form of yellow needles (0.55 g., 77%) that melted at 87–88° (literature[7] 88°) by crystallization from acetic acid.

Anal. Calcd. for $C_{12}H_{10}O_2$: C, 77.4; H, 5.4. Found: C, 76.9; H, 5.5.

We thank the Graduate School of the University of Minnesota for a grant from the Fluid Research Fund.

(7) Kruber and Schade, *Ber.*, **69**, 1722 (1936).

Summary

A series of reactions has been described which appears to constitute a general method for the preparation of 1,4-naphthoquinones and hydroquinones which contain a hydrocarbon residue in position 2 and which bear a hydrogen, a hydroxyl or a carbethoxyl in position 3.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

p-Cymene Studies. IV. Mononitration of 2-Amino-*p*-cymene. Preparation of 3-Amino-*p*-cymene and *o*- and *p*-Cymylenediamine

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Of the three possible nitro-2-amino-*p*-cymenes, only one has been reported formed in the nitration of 2-amino-*p*-cymene liquid isomer obtained by Wheeler and Brooks.[1,2] We now find that the large amount of tarry by-product in this reaction consists almost exclusively of a solid isomer. Wheeler and Brooks claimed their liquid product to be 2-amino-5-nitro-*p*-cymene, which would make the solid product the 2-amino-3-nitro-*p*-cymene. In our investigation of these compounds the following proof is given that the liquid isomer (I) is 2-amino-3-nitro-*p*-cymene and the solid isomer (II) is 2-amino-5-nitro-*p*-cymene. Product I on reduction gave an unknown diamine in which the *ortho* position of the amino groups is proved by their ready condensation with benzil and phenanthraquinone, and by its conversion to a benzimidazole on heating with glacial acetic acid or atmospheric distillation of its diacetyl derivative. Product II when reduced to the diamine could be oxidized to thymoquinone.

The 2-acetamino-*p*-cymene is extremely diffi-

(1) Wheeler and Brooks, THIS JOURNAL, **49**, 2832–2834 (1927).
(2) Wheeler and Cutlar, *ibid.*, **49**, 2819–2822 (1927).

cult to purify for nitration purposes. Nitration of this acetyl derivative gave 52% 2-amino-3-nitro-*p*-cymene and 48% 2-amino-5-nitro-*p*-cymene. The nitration of 2-amino-*p*-cymene sulfate gave approximately 60% 2-amino-3-nitro-*p*-cymene and 40% 2-amino-5-nitro-*p*-cymene.

In this work 2-formylamino-*p*-cymene was used instead of the corresponding acetyl derivative, because of its ease of purification and subsequent ease of hydrolysis of the formyl groups from the isomeric nitroamines. Further, it gave the isomeric nitroamines in a practically pure state after fractionation, thus eliminating any purification through acyl derivatives. Nitration gave 70% of 2-amino-3-nitro-*p*-cymene and 30% of 2-amino-5-nitro-*p*-cymene.

Reduction of the nitroamines with zinc dust and sodium hydroxide gave the corresponding cymylenediamines in excellent yield. Statements as to the instability of *p*-cymylenediamine were found to be somewhat misleading. This compound was isolated in the pure state and found to deteriorate only very slowly in the presence of light. In aqueous ethanol solution this compound is more rapidly destroyed. The elaborate vacuum distillation apparatus employed by Wheeler and Bost[3] for the isolation of this diamine was found to be unnecessary.

Experimental[4,5]

2-Formylamino-*p*-cymene (I).—Nitration and reduction were carried out according to our published methods.[6] All *p*-toluidine was removed from the crude 2-amino-*p*-cymene by repeated fractionation *in vacuo*. A solution of 149 g. (1.0 mole) of 2-amino-*p*-cymene and 90 g. (1.76 moles) of formic acid (90%) was refluxed for two hours. (The excess of formic acid was used to prevent violent bumping.) The product after shaking with 300 ml. of water and cooling gave the formyl derivative as an oil which rapidly solidified. It was crystallized twice from ethanol, forming colorless needles of m. p. 108.8–109.4°. It is very soluble in cold concentrated sulfuric acid or chloroform, quite soluble in ether or acetone, slightly soluble in hot water, and practically insoluble in cold water.

Anal. Calcd. for $C_{11}H_{15}NO$: N, 7.90. Found: N, 7.95.

Nitration.—100 g. of I (0.565 mole) of m. p. 108.8–109.4° was dissolved in 400 g. of sulfuric acid (sp. gr. 1.84). To this solution at 0° was added drop by drop with stirring a previously cooled nitrating acid consisting of 56 g. (0.613 mole) of nitric acid (sp. gr. 1.42) and 100 g. of sulfuric acid (sp. gr. 1.84). After the addition of all the nitrating acid stirring was continued for ten minutes. The mixture was poured with efficient stirring into about 0.5 kg. of crushed ice in 0.5 kg. of water. The product was a yellow, sticky, amorphous mass which became hard and crystalline after several hours. It was filtered, washed with cold water and air dried. The filtrate was extracted with 50 ml. of chloroform and the latter evaporated; total yield, 113 g. (90%).

Hydrolysis.—The crude formyl-nitroamines (113 g.) were refluxed for one hour with 150 ml. of 30% sodium hydroxide solution. The red nitroamine layer was washed with water; the sodium hydroxide layer extracted with benzene (25 ml.), and the latter evaporated off; total yield, 98.2 g. (99%).

Separation of Isomeric Nitroamines.—The nitroamines (98.2 g.) were fractionated very slowly three times in a 150 ml. well-lagged Vigreux flask of 16-cm. column resulting in the following fractions: (1) 0.8 g. of a light yellow liquid of b. p. 65–67° (1 mm.); (2) 64.5 g. of an orange-red liquid of b. p. 114–116° (1 mm.); and (3) 26.6 g. of a yellow solid b. p. 144–148° (1 mm.), m. p. 57–60°. The residue in the flask was 4.5 g. At this low pressure superheating very easily occurs; consequently, to avoid this, fractionation must be executed slowly; approximately eight hours was used.

Fraction (1) was acetylated by refluxing with 5 ml. of acetic anhydride for one hour. The resulting product (after washing with water and refrigerating at 0°) remained liquid. It was boiled for one hour with 20 ml. of concentrated hydrochloric acid made alkaline with sodium hydroxide solution, and extracted with benzene. The free base was refluxed with 5 ml. of formic acid (90%) for one hour; it was crystallized once from ethanol and boiled with Norite in ethanol; m. p. 108.8–109.4° (mixed m. p. with authentic 2-formylamino-*p*-cymene was the same).

2-Amino-3-nitro-*p*-cymene (II).—Fraction (2), 64.5 g., was acetylated by refluxing with equivalent acetic anhydride for three hours. The product consisted of only one **acetylderivative**, as colorless needles of m. p. 167.6–167.8° from ethanol–ether mixture. It was crystallized by dissolving in ethanol, diluting with ether and cooling to 0°. A total of 65 g. of this acetyl derivative was isolated; the residue of crystallization amounted to 0.6 g. Thus the II taken for acetylation was practically pure.

Anal. Calcd. for $C_{12}H_{16}N_2O_3$: N, 11.86. Found: N, 11.82.

This acetyl derivative was hydrolyzed by refluxing with 100 ml. of concentrated hydrochloric acid for two hours. The mixture was made alkaline with sodium hydroxide solution and after washing with water was distilled. II is an orange-red liquid of sweet taste and of b. p. 142.9° (5 mm.), 158.8° (10 mm.), 175.6° (20 mm.) and at atmospheric pressure it is decomposed. The salts formed with hydrochloric, nitric, or sulfuric acid are all hydrolyzed by cold water.

Its formyl **derivative** was prepared by refluxing 5 g. of II with 10 g. of formic acid (90%) for five hours. (After

(3) Wheeler and Bost, THIS JOURNAL, **50**, 2000 (1928).

(4) All melting points are corrected and were determined using Brothcom total immersion thermometers graduated in 0.2° (immediately after crystallization and air drying); this was found to be necessary since many of the compounds, such as the acyl derivatives of the nitroamines, were found to be transformed upon standing into modifications which for some of the compounds have different melting points.

(5) Analyses for nitrogen by micro-Dumas using dry-ice as a source of pure carbon dioxide.

(6) Kobe and Doumani, *Ind. Eng. Chem.*, **31**, 257 (1939); Doumani and Kobe, *ibid.*, **31**, 264 (1939).

two hours refluxing there still remained unreacted amine.) It was crystallized from ethanol in colorless needles which soften at 128.0° and melt at 139.6–140.0°.

Anal. Calcd. for $C_{11}H_{14}N_2O_3$: N, 12.61. Found: N, 12.60.

Its **benzoyl derivative** was prepared by heating 5 g. of 2-amino-3-nitro-*p*-cymene with 10 g. of benzoyl chloride for five minutes at 90°. It crystallizes from ethanol as colorless needles of m. p. 193.4–193.8°.

Anal. Calcd. for $C_{17}H_{18}N_2O_3$: N, 9.39. Found: N, 9.33.

***o*-Cymylenediamine (III).**—Thirty-five grams of II, 35 ml. of ethanol, and 30 ml. of 30% sodium hydroxide solution was shaken with the addition of 50 g. of zinc dust in such portions that the solution gently refluxed. After the addition of all the zinc dust it was further refluxed for one hour giving a light brown solution. The excess zinc dust was filtered off in the hot, and the filtrate rapidly cooled, causing the diamine to crystallize out. (In alkaline solution upon standing in the presence of air this compound is slightly oxidized to a reddish dye very soluble in ethyl ether.) This *o*-diamine forms hard, well-defined, colorless, rhombic crystals from ethanol of m. p. 95.0–95.8°. It remains practically colorless on long standing in the presence of light. It is very soluble in acetone, ethyl ether, chloroform, or benzene, and practically insoluble in petroleum ether; yield 26 g. (88%).

Anal. Calcd. for $C_{10}H_{16}N_2$: N, 17.06. Found: N, 17.04.

***o*-Diacetylcymylenediamine (IV).**—Fifteen grams of III was dissolved in 30 ml. of acetic anhydride. The diacetyl derivative crystallized out upon cooling; colorless needles of constant m. p. 235.1–235.3° were obtained after one crystallization from ethanol. Refluxing 5 g. of III with 10 ml. of acetic anhydride for one hour gave a mixture of IV and the anhydro base (V).

Anal. Calcd. for $C_{14}H_{20}N_2O_2$: N, 11.28. Found: N, 11.23.

2,7-Dimethyl-4-isopropyl-benzimidazole (V). A.—Ten grams of IV was distilled at atmospheric pressure, b. p. 326–327° (uncor.). The distillate was crystallized by dissolving in the minimum volume of warm benzene and diluting with two volumes of warm petroleum ether. Upon cooling colorless crystals of m. p. 179.5–179.9° were obtained. This benzimidazole is very soluble in ethanol, ethyl ether, chloroform, or benzene, slightly soluble in hot water or petroleum ether, and practically insoluble in cold water. It readily forms salts with dilute hydrochloric, nitric, sulfuric, or acetic acid.

Anal. Calcd. for $C_{12}H_{16}N_2$: N, 14.88. Found: N, 14.81.

B.—2.5 g. of III was refluxed for one hour with 10 g. of glacial acetic acid. It was made alkaline with dilute sodium hydroxide solution, clarified by boiling with Norite in benzene, and recrystallized as in A, above. A mixed m. p. with the above compound in A was not depressed.

2,3-Diphenyl-5-isopropyl-8-methylquinoxaline.—3.3 g. of III, 4.2 g. of benzil, and 30 ml. of ethanol were refluxed together for fifteen minutes. The quinoxaline separated out and was recrystallized from benzene–ethanol mixture (1:2); colorless crystals, m. p. 136.7–137.3°. This compound gives a blood red coloration when treated with a drop of concentrated sulfuric acid; upon dilution, the color becomes yellow. Concentrated hydrochloric acid gives a yellow coloration.

Anal. Calcd. for $C_{24}H_{22}N_2$: N, 8.27. Found: N, 8.14.

10-Isopropyl-13-methyldibenzophenazine.—0.8 g. of III, 1 g. of phenanthraquinone, and 20 ml. of glacial acetic acid were refluxed for fifteen minutes. The product was insoluble and was crystallized from benzene as light yellow needles of m. p. 181.2–181.4°. This compound gives a purplish-red coloration when treated with a drop of concentrated sulfuric acid. Concentrated hydrochloric acid gives a yellow coloration.

Anal. Calcd. for $C_{24}H_{20}N_2$: N, 8.33. Found: N, 8.26.

2-Amino-5-nitro-*p*-cymene (VI).—Fraction (3), 26.6 g., was recrystallized from ethanol as canary yellow needles of m. p. 66.6–67.6°. A total of 24.8 g. of VI was isolated; only 1.1 g. of impure amine could not be purified in this manner; however, upon acetylation with acetic anhydride it proved to be the 2-acetamino-5-nitro-*p*-cymene. Thus, the 26.6 g. of nitroamine taken for crystallization was practically pure. Like II its salts with hydrochloric, nitric, or sulfuric acid are all hydrolyzed by cold water; unlike it, however, it is tasteless.

Anal. Calcd. for $C_{10}H_{14}N_2O_2$: N, 14.42. Found: N, 14.48.

The **acetyl derivative**, prepared by refluxing with equivalent acetic anhydride for three hours, was crystallized once from ethanol and boiled with Norite in ethanol, giving colorless needles of m. p. 142.8–143.2°.

Anal. Calcd. for $C_{12}H_{16}N_2O_3$: N, 11.86. Found: N, 11.81.

Its **formyl derivative** was prepared by refluxing 5 g. of the amine with 20 ml. of formic acid (90%) for four hours; yellow crystals from ethanol, m. p. 101.6–102.2°.

Anal. Calcd. for $C_{11}H_{14}N_2O_3$: N, 12.61. Found: N, 12.59.

Its **benzoyl derivative**, prepared by heating the amine with a 20% excess of benzoyl chloride at 90° for fifteen minutes, crystallized from ethanol as light yellow, monoclinic crystals of m. p. 139.0–139.4°.

Anal. Calcd. for $C_{17}H_{18}N_2O_3$: N, 9.39. Found: N, 9.42.

***p*-Cymylenediamine (VII).**—19.4 g. (0.1 mole) of VI dissolved in 50 ml. of ethanol was mixed with 25 ml. of 40% sodium hydroxide solution and treated with 30 g. of zinc dust in such portions that the solution gently refluxed when shaken. Refluxing was continued for one hour after the addition of all the zinc dust; the excess zinc dust was filtered off, the ethanol evaporated off, the brown amine layer separated from the caustic layer and the amine distilled, b. p. 120–125° (1 mm.) uncor. The colorless amine rapidly turned yellow. It was recrystallized by dissolving in the minimum benzene (1 vol.) in the hot, diluting with warm petroleum ether (2 vols.), and cooling, giving large yellow coarse crystals that rapidly turned brown; m. p. 50.0–50.5°; yield 14.1 g. (86%).

Anal. Calcd. for $C_{10}H_{16}N_2$: N, 17.06. Found: N, 17.01.

p-Diacetylcymylenediamine.—Two grams of VII was heated with 10 ml. of acetic anhydride at 90° for five minutes. Crystallization from benzene gave m. p. 262.0–262.2°.

Anal. Calcd. for $C_{14}H_{20}N_2O_2$: N, 11.28. Found: N, 11.27.

Thymoquinone.—Half a gram of finely crushed VII was shaken for five minutes with 50 ml. of 50% ferric chloride solution at room temperature. The thymoquinone was insoluble; it was filtered off and crystallized from petroleum ether; m. p. 45.6–46.0° mixed m. p. with thymoquinone[7] prepared from thymol was the same.

3-Nitro-*p*-cymene (VIII). A.—From II: 8 g. of powdered sodium nitrite was dissolved in 160 g. of sulfuric acid (sp. gr. 1.84) below 40°. Very slowly at 35–40° was added 20 g. of II to avoid the precipitation of the insoluble amine sulfate. Stirring was continued for fifteen minutes after which a drop when poured in water gave none of the colored nitroamine. To this mixture was slowly added 300 ml. of absolute ethanol with vigorous shaking; the resulting mixture was refluxed for one hour. Steam distillation gave some phenolic substance (removed by washing with dilute sodium hydroxide solution) and VIII; yield 9.7 g. (52%). VIII is a light yellow liquid of b. p. 116.7 (10 mm.), b. p. 133.5 (20 mm.), and at atmospheric pressure it is decomposed.

B.—From VI: 20 g. of VI was dissolved in 20 ml. of glacial acetic acid and diazotized exactly as in A. The product consisted mostly of a phenolic residue in the steam distillation flask. The yield of VIII was 2.3 g.

C.—Twenty grams of the mixture of isomeric nitroamines in the proportion as formed by the nitration of I was diazotized and treated as in A, with the further addition of 5 g. of freshly reduced copper as a suspension in the absolute ethanol; yield 9.8 g. (53%).

3-Amino-*p*-cymene (IX).—The VIII in A and B above, were separately reduced with iron powder and hydrochloric acid.[6] Both amines gave the same formyl derivative by refluxing with twice the volume of formic acid (90%) for two hours. 3-Formylamino-*p*-cymene forms colorless needles from ethanol of m. p. 106.2–106.6°. There was a depression of the melting point when admixed with I.

Anal. Calcd. for $C_{11}H_{15}NO$: N, 7.90. Found: N, 7.83.

3-Amino-*p*-cymene is a colorless liquid of b. p. 105.7° (10 mm.), 122.1° (20 mm.), 240.2° (760 mm.).

Thymol.—Five grams of IX was dissolved in 50 ml. of 5% sulfuric acid and diazotized with the exact equivalent of sodium nitrite dissolved in 10 ml. of water. It was steam distilled, extracted with dilute sodium hydroxide, and acidified, giving thymol of m. p. 47–49° from petroleum ether. The m. p. was raised when mixed with synthetic thymol from *m*-cresol and isopropyl alcohol.

Summary

1. Nitration of 2-formylamino-*p*-cymene gives 70% of 2-amino-3-nitro-*p*-cymene and 30% of 2-amino-5-nitro-*p*-cymene. Nitration of 2-acetylamino-*p*-cymene gives 52 and 48%, respectively, of the above nitroamines.

2. Quantitative separation of the isomeric nitroamines can be effected by fractionation *in vacuo*.

3. The isomeric cymylenediamines can be obtained in excellent yield from the nitroamines by reduction with zinc dust and sodium hydroxide solution.

4. The nitroamine that has previously been described as 2-amino-5-nitro-*p*-cymene has been proved to be 2-amino-3-nitro-*p*-cymene.

(7) Kremers, Wakeman, and Hixon, *Org. Syntheses*, **6**, 92 (1926).

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Alkaline Hydrolysis of Condensation Products of Hydantoin with Aldehydes[1]

BY HENRY R. HENZE, WILLIAM B. WHITNEY AND MARGARET A. EPPRIGHT

The condensation of aldehydes with the methylene hydrogens in —X—CH_2—CO— has been a valuable reaction for synthetic purposes following Perkin's[2] condensation of salicylic aldehyde and sodium acetate in the presence of acetic anhydride. This reaction has since been modified and widely applied. Plöchl and Wolfrum[3] were the first to employ it in connection with condensations involving the —NH—CH_2—CO— grouping. Initially, Plöchl used glycine but later he found that hippuric acid, the benzoyl derivative of glycine, gave much better results. Erlenmeyer[4] studied the chemical behavior of these condensation products of hippuric acid and obtained alpha amino acids by their reduction and *subsequent* hydrolysis.

Wheeler and Hoffman[5] further modified the

(1) Presented before the Division of Organic Chemistry at the 96th meeting of the American Chemical Society at Milwaukee, Wis., Sept. 5–9, 1938.

(2) Perkin, *Chem. News*, **32**, 258 (1875).

(3) Plöchl, *Ber.*, **16**, 2815 (1883); Plöchl and Wolfrum, *ibid.*, **18**, 1183 (1885).

(4) Erlenmeyer, jun., *Ann.*, **271**, 137 (1892); **275**, 1 (1893); *Ber.*, **30**, 2976 (1897).

(5) Wheeler and Hoffman, *Am. Chem. J.*, **45**, 368 (1911).