nitrosochloride, colorless prisms from chloroform–methanol, m.p. 133–134° dec.

Anal. Calcd. for $C_{12}H_{14}ClNO$: Cl, 15.9. Found: Cl, 15.9.

When the acetic acid–methanol mother liquor from the above preparation was poured into one liter of water, there was deposited an oil which soon solidified. This material was ground up with ligroin and then with dilute sodium carbonate and crystallized from alcohol, giving 9 g. (16%) of phenylcyclohexenone oxime. Larger scale (2–3×) preparations gave less nitrosochloride (45–40%) and more oxime (28–35%).

To a stirred boiling suspension of 175 g. of the nitrosochloride in 600 ml. of 95% ethanol was added 125 g. of 85% potassium hydroxide in 150 ml. of water. A clear solution resulted, except for precipitated potassium chloride, after 2.25 hours, but boiling was continued for three hours. The mixture was then neutralized with acetic acid, cooled, and filtered. The precipitate was washed with water, giving 113 g. (77%) of nearly pure **2-phenyl-2-cyclohexenone oxime**, and 4.6 g. more was obtained from the filtrates. Crystallization from alcohol gave coarse colorless needles, m.p. 157–158°.

Anal. Calcd. for $C_{12}H_{13}NO$: C, 77.0; H, 6.9. Found: C, 77.0; H, 7.1.

Reduction of 1 g. of the oxime with 2 g. of sodium and 25 ml. of butyl alcohol gave 0.9 g. of **2-phenylcyclohexylamine** a colorless oil, b.p. 137–139° at 14 mm. **The hydrochloride** had m.p. 250–254° (Found: C, 67.8; H, 8.6; N, 6.9, $C_{12}H_{18}ClN$ requires C, 68.2; H, 8.5; N, 6.6). **The benzoyl derivative** formed fine needles from alcohol, m.p. 183–184° (Found: C, 82.5; H, 8.0. $C_{19}H_{21}NO$ requires C, 82.1; H, 7.6).

A solution of 180 g. of phenylcyclohexenone oxime in 360 ml. of concentrated hydrochloric acid and 180 ml. of water was warmed on a water-bath for 30 minutes. The mixture was then cooled and filtered, and the solid was washed with water and dried. The filtrate was diluted with 3 l. of water, which caused 22 g. of unchanged oxime to precipitate. There was obtained 140 g. of crude phenylcyclohexenone, a yield of 84%, or 96% on the basis of oxime actually consumed. Distillation gave 127 g., b.p. 169–171° at 14 mm., of pure product, colorless needles from alcohol, m.p. 94–95° (reported[1] 95–95.5°).

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.7; H, 7.0. Found: C, 83.3; H, 7.2.

As a derivative characteristic of an α,β-unsaturated ketone,[4] **2-phenyl-3-*p*-toluenesulfonylcyclohexanone** was prepared by boiling 0.7 g. of phenylcyclohexenone with 0.7 g. of *p*-toluenesulfinic acid in 5 ml. of alcohol for two hours; it formed long white needles from alcohol, m.p. 158–159° with slow gas evolution.

Anal. Calcd. for $C_{19}H_{20}O_3S$: C, 69.5; H, 6.2. Found: C, 69.5; H, 6.5.

3-Oxo-2-phenylcyclohexaneacetic Acid (IV).—A mixture of 126 g. of phenylcyclohexenone, 100 g. of methyl malonate (ethyl malonate did not react under similar conditions), and 100 ml. of methanol was boiled, then cooled to 40° and treated with a solution of 1 g. of sodium in 15 ml. of methanol. The mixture became homogeneous after nine minutes, and its temperature rose (39 to 47.7°) during 13 minutes, then began to fall slowly. After ten hours, 700 ml. of water containing 70 g. of sodium hydroxide was added, and the mixture was boiled under reflux for 30 minutes. It was then cooled, and unchanged phenylcyclohexenone (60–65 g.) was removed by filtration. The filtrate was concentrated somewhat, 400 ml. of dilute methanol being distilled, and then acidified with dilute sulfuric acid. The sirupy dibasic acid (102 g.) was separated using 150-, 100- and 50-ml. portions of ether, and heated at 220° for a few minutes. The residue (80 g., 96%) was crystallized from benzene and dried for six hours in air. There was obtained 82 g. of white needles that sintered at 95° and melted at 104–105° with effervescence; this was a complex of the acid with benzene (Found: C_6H_6, 24.4. $C_{14}H_{16}O_3 + C_6H_6$ requires C_6H_6, 25.1). From dilute acetic acid, solvent-free needles were obtained, m.p. 124–125° (reported[2] 124–125°).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.4; H, 6.9; neut. equiv., 232. Found: C, 72.0; H, 6.9; neut. equiv., 232.

A mixture of 10 g. of the keto-acid IV, 25 ml. of ethanol and 5 ml. of sulfuric acid was boiled for one hour, then poured into dilute soda solution. There was obtained 2.5 g. of unchanged acid, and 8.1 g. of **ethyl 3-oxo-2-phenylcyclohexaneacetate**, plates from alcohol, m.p. 73–75°; b.p. 205–210° at 13 mm.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.9; H, 7.7. Found: C, 74.3; H, 7.8.

4-Benzal-3-oxo-2-phenylcyclohexaneacetic Acid (VI).—A solution of 15.5 g. of solvated oxophenylcyclohexaneacetic acid and 2.5 g. of sodium hydroxide in 50 ml. of water was boiled to remove benzene, then cooled to 45°, treated with 5.5 g. of benzaldehyde, and shaken for 30 minutes. The mixture was then boiled for 15 minutes and finally acidified, yielding an oil that became solid when it was rubbed with ether. Crystallization from 75% acetic acid gave 9.5 g. of small pale yellow prisms, m.p. 151–153°.

Anal. Calcd. for $C_{21}H_{20}O_3$: C, 78.8; H, 6.3. Found: C, 79.0; H, 6.3.

When 8.5 g. of VI was boiled for three hours with 40 ml. of ethanol containing 2 ml. of sulfuric acid, there was obtained 8.9 g. of the ethyl ester of VI, pale yellow prisms from alcohol and then from benzene–ligroin, m.p. 92–94°.

Anal. Calcd. for $C_{23}H_{24}O_3$: C, 79.3; H, 6.9. Found: C, 79.3; H, 6.9.

1,2,11,12-Tetrahydrophenanthrene-4(3),9(10)-dione (VII).—A solution of 1 g. of solvated IV in 3 ml. of 96% sulfuric acid was heated in a boiling water-bath for 30 minutes, then poured onto ice and ether. The product was washed with dilute soda solution and distilled, giving 0.35–0.43 g. of pale yellow oil, b.p. 215–220° at 14 mm., that crystallized when it was rubbed with ether. Recrystallization of 0.6 g. from benzene–ligroin and then from dilute acetic acid gave 0.25 g. of faintly colored prisms, m.p. 94–95°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.5; H, 6.6. Found: C, 78.5; H, 6.6.

The author thanks Mr. L. A. Errede for most of the analyses reported in this note.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS 14, MINN.

RECEIVED FEBRUARY 5, 1951

---

(4) E. P. Kohler and M. Reimer, *Am. Chem. J.*, **31**, 163 (1904).

The Use of C^{14}-Labeled Formaldehyde in the Mannich Reaction[1,2,3]

BY ALBERT V. LOGAN, JOHN L. HUSTON AND DONALD L. DORWARD

In the course of a study of the mechanism of the Mannich reaction C^{14} labeled paraformaldehyde was incorporated in a Mannich base to determine the possibility of the transposition of the carbon atoms. The reaction investigated involved the condensation of acetophenone, radioactive paraformaldehyde[4] and dimethylamine hydrochloride. The Mannich base, βC^{14}-β-dimethylaminopropiophenone, was pyrolyzed by steam and the resulting vinyl phenyl ketone subjected to ozonolysis. The ozonide was hydrolyzed and the products, phenyl glyoxal and formaldehyde, were separated. The radioactivity of each product was determined.

If no transposition of carbon atoms occurs the formaldehyde should contain all of the C^{14}. We found that the phenyl glyoxal monohydrate counted as the pure compound showed an initial activity

---

(1) Published with the approval of the Monograph Publications Committee, Oregon State College, as Research Paper No. 174, School of Science, Department of Chemistry.

(2) The work reported here was done with the aid of a grant from the Research Corporation, New York, N. Y.

(3) This note is based upon a thesis submitted by Donald L. Dorward in partial fulfillment of the requirements for the degree of Master of Science at Oregon State College, June, 1949.

(4) C. E. Spencer, thesis submitted to Oregon State College, 1949.

of 1.4 c./m./mg. corrected for background and self absorption. The activity decreased to 0.7 c./m./mg. after leaching with water and recrystallizing. We did not obtain a completely inactive sample of phenyl glyoxal monohydrate but the rapid decrease in activity led us to believe the activity found was due to occluded formaldehyde. The formaldehyde counted as the dimedon derivative showed a specific activity of 3 c./m./mg.

The results of the experiment indicate that there is no transposition of the carbon atoms during the formation of the Mannich base. Work is underway with a higher activity formaldehyde to determine if the unreacted formaldehyde is held in a complex with the acetophenone.

Experimental

The reaction conditions for the preparation of β-C^{14}-β-dimethylaminopropiophenone were changed somewhat from those normally used.[5] On the basis of work done by Plati and Wenner,[6] it was believed to be possible to improve the yield of the base by changing the solvent conditions. A 50-50 mixture of acetophenone and 95% ethanol was finally adopted.

The Mannich base was prepared by heating, under reflux, 1.84 g. (0.06 mole) of radioactive paraformaldehyde and 9.70 g. (0.12 mole) of dimethylamine hydrochloride in a solution of 10 ml. of acetophenone and 10 ml. of 95% ethanol. After heating for two hours, the solution was seeded and chilled overnight. The product, recrystallized from acetone, weighed 6.62 g. (0.031 mole). The yield was 51% based upon the radioactive paraformaldehyde; uncorrected m.p. 155-157° (reported 157-158°).

The Mannich base was subjected to steam distillation and the resulting vinyl phenyl ketone was extracted from the distillate with chloroform. The chloroform was removed by distillation and the unsaturated ketone was dissolved in 100 ml. of glacial acetic acid. The solution was heated to 80° and treated with ozone for a period of four hours. The material was poured into 100 ml. of water with 2 g. of zinc added to prevent oxidation. The precipitate of phenyl glyoxal monohydrate was removed by filtration. A saturated ethanol solution of 5 g. of dimedon was added to the filtrate. The mixture was seeded and chilled to recover the methylene-bis-dimedon (320 mg. m.p. 182-185°).

---

(5) C. Mannich and G. Heilner, *Ber.*, **55**, 356 (1922).

(6) J. T. Plati and W. Wenner, *J. Org. Chem.*, **14**, 543 (1949).

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON

RECEIVED MAY 29, 1950

Absorption Spectra of Some Substituted Benzoquinones

BY CATHERINE M. MARTINI AND FREDERICK C. NACHOD

The ultraviolet absorption spectra[1] of a series of substituted benzoquinones were determined in solutions at various *p*H levels (Sørensen buffer, *p*H 7, 0.01 *N* NaOH solution, and 0.01 *N* HCl solution).

The spectra of the 2- and the 2,5-bis-alkylaminobenzoquinones in *p*H 7 buffer showed marked similarities, as illustrated by (1) 2,5-bis-(methylamino)-benzoquinone; (2) 2,5-bis-(*n*-butylamino)-benzoquinone; (3) 2,5-bis-[3-(1-piperidyl)-propylamino]benzoquinone; (4) 2-[3-(1-piperidyl)-propylamino]-benzoquinone methyl bromide and (5) 2-[3-(1-piperidyl)-propylamino]-benzoquinone in Fig. 1.[2]

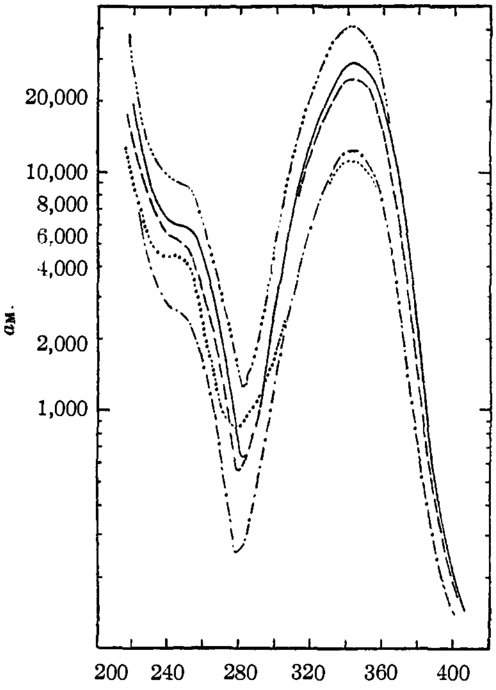

Fig. 1.—(1) —··—···—, 2,5-bis-(methylamino)-benzoquinone; (2) ———, 2,5-bis-(*n*-butylamino)-benzoquinone; (3) — — —, 2,5-bis-[3-(1-piperidyl)-propylamino]benzo-*quinone*; *(4)*— —— - —, *2-[3-(1-piperidyl)-propylamino]*-benzoquinone methyl bromide; (5) - - - - - - - - - - -, 2-[3-(1-piperidyl)-propylamino]-benzoquinone.

All the spectra have maxima at 343 mμ, minima at 280 mμ and inflection points at 244 mμ, and differ only in the hyperchromic molar absorbency (a_M) produced by the bis compounds. Contrary to what might be expected there were no changes produced in the spectra when determined in basic or acidic solutions.

The situation, however, was found to be quite different with 2- and 2,5-bis-dialkylaminobenzoquinones. When the spectrum of 2-hydroxy-5-dimethylaminobenzoquinone[3] was determined in water solution, *p*H 6; or in 0.01 *N* NaOH solution, *p*H 13, a maximum was observed at 318 mμ. In 0.01 *N* HCl solution, *p*H 2, the expected hypsochromic shift due to prototropic changes was observed producing a maximum at 282 mμ. In order to demonstrate, qualitatively, the equilibrium involved above, the spectrum was determined in water and the maximum at 318 mμ was obtained. When the *p*H of this solution was adjusted to 2.0 with concentrated HCl, the hypsochromic shift to 282 mμ was obtained.

When the *p*H was once again adjusted to 7 with alkali, the expected bathochromic shift took place and the compound once again exhibited a maximum at 318 mμ. The same experiment was attempted with 2,5-bis-(dimethylamino)-benzoquinone.[2] In *p*H 7 buffer and 0.01 *N* NaOH solu-

---

[1] The spectra were determined with a Beckman quartz spectrophotometer, Model DU, Serial No. D-337, using a minimal slit width and 10 mm. quartz cells.

[2] C. J. Cavallito, A. E. Soria and J. O. Hoppe, THIS JOURNAL, **72**, 2661 (1950).

[3] F. Kehrmann, *Ber.*, **23**, 897 (1890).