[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LUTHER COLLEGE]

A Rearrangement of *p*-Benzoquinonedioxime to *p*-Nitroaniline[1]

A. M. DOCKEN, G. D. BURT, R. D. ELLEFSON, AND D. L. OSTERCAMP

Received August 28, 1958

When p-benzoquinonedioxime is heated in polyphosphoric acid at 130–140° it rearranges to p-nitroaniline. Two bis(benzenesulfonyl) derivatives of p-benzoquinonedioxime have been prepared.

The possibility that a Beckmann rearrangement of p-benzoquinonemonoxime would lead to a seven-membered, heterocyclic compound related to tropolone stimulated a reexamination[2–4] of the yellow product formed by heating the benzenesulfonyl derivative of p-benzoquinonemonoxime in pyridine.[5] This yellow product, however, proved to be p-azoxyphenol, not a Beckmann rearrangement product.

Horning and co-workers discovered that polyphosphoric acid is an efficient and specific agent which effects the Beckmann rearrangement of oximes that had not previously been observed to rearrange with conventional catalysts.[6] We thought it desirable, therefore, to investigate the action of polyphosphoric acid on both the monoxime and the dioxime of p-benzoquinone.

When p-benzoquinonemonoxime was heated in polyphosphoric acid, extensive decomposition occurred with evolution of gaseous products. Only tars were found in the diluted reaction mixture. The benzenesulfonate of the monoxime in polyphosphoric acid either at elevated temperatures or at room temperature, underwent no reaction other than tar formation.[7] A portion of the starting material was recovered in most cases either as the monoxime or as the benzenesulfonate.

The dioxime of p-benzoquinone proved to be much more stable in polyphosphoric acid. This substance could be recovered nearly quantitatively from a reaction mixture which had been heated briefly to 130°. Heating the dioxime with polyphosphoric acid for 90 minutes produced p-nitroaniline in 40–45% yield. A small amount of the dioxime was also recovered. The p-nitroaniline was identified by conversion to p-nitroacetanilide and p-nitrobenzenesulfonanilide. Mixed melting points with authentic samples were used in each case. The recovered dioxime was identified by melting point and formation of dinitrosobenzene by potassium ferricyanide oxidation.[8]

Several unsuccessful attempts were made to promote the rearrangement to p-nitroaniline by the use of sulfuric acid. In concentrated acid or in non-aqueous dilute solutions decomposition was the only reaction observed.

The bis(benzenesulfonate) of the dioxime was next investigated in view of the increased ease with which certain oxime sulfonates undergo the Beckmann rearrangement.[9] The synthesis of the bis(benzenesulfonyl) derivative (m.p. 175–178°) by the action of benzenesulfonylchloride in pyridine solution was reported by Beckmann and Liesche.[5] By the same procedure we obtained a product from which two white substances were separated by fractional crystallization. These appear to be derivatives of the syn and anti forms of the dioxime. One form melts with decomposition at 157–158°, the other with decomposition at 196–197° (203–204° in a preheated bath).

These two substances are considered to be geometrical isomers on the basis of the carbon, hydrogen, and nitrogen analyses, and on the basis of a comparison of the ultraviolet absorption spectra with those of p-benzoquinonedioxime and its diacetate. The ultraviolet spectrum of each of these substances has a single, broad absorption maximum: p-benzoquinonedioxime, 318 mμ; the diacetate, 303 mμ; the higher melting bis(benzenesulfonate), 307 mμ, ϵ = 48,300 in CH_2Cl_2; the lower melting, 305 mμ, ϵ = 39,800 in CH_2Cl_2.

In the study of the effect of polyphosphoric acid on the bis(benzenesulfonate) of the dioxime a mixture of the two forms was used. This disulfonate required a higher temperature for the reaction than the dioxime itself, and from the reaction mixture p-nitroaniline was obtained in low yield with a small amount of the dioxime.

EXPERIMENTAL[10]

p-Benzoquinonemonoxime. The monoxime was prepared by acidification of a solution of p-nitrosophenol sodium salt (EKC 2354). The dried, impure p-nitrosophenol was dissolved in ether and treated with decolorizing carbon until a pure green solution was obtained. This solution was diluted with an equal volume of petroleum ether, b.p. 35–60°, and

---

[1] This work was supported by a Frederick Gardner Cottrell Grant from the Research Corporation.

[2] R. A. Raphael and E. Vogel, *J. Chem. Soc.*, 1958 (1952).

[3] N. J. Leonard and J. W. Curry, *J. Org. Chem.*, **17**, 1071 (1952).

[4] Unpublished work done in this laboratory.

[5] E. Beckmann and O. Liesche, *Ber.*, **56**, 1 (1923).

[6] E. C. Horning, V. L. Stromberg, and H. A. Lloyd, *J. Am. Chem. Soc.* **74**, 5153 (1952).

[7] J. L. Tveten performed a part of the investigation of this reaction.

[8] R. Nietski and F. Kehrmann, *Ber.*, **28**, 342 (1895).

[9] B. Jones, *Chem. Revs.*, **35**, 335 (1944).

[10] All melting points are uncorrected.

cooled to −20°. The crystalline material obtained was pale tan in color and melted at 137° with decomposition.

p-Benzoquinonedioxime was prepared by the method of J. H. Trepagnier.[11] Decomposition of our samples began in the range 230° to 240°.

p-Benzoquinonedioxime to p-Nitroaniline. Three g. (0.0217 mole) of the dioxime and 170 g. of polyphosphoric acid (Victor Chemical Works, 115% ortho equivalent) in a 200 ml., 3-necked flask were heated by an oil bath to 133–137° for 90 min. with rapid stirring. The reaction mixture was poured over a 400–500 ml. volume of crushed ice. The purple, aqueous solution was filtered by suction to remove a small amount of black, gummy material and then extracted 12–14 times with 50 ml. portions of ether.

The combined ether extracts were washed with two portions of 10% sodium hydroxide, dried over anhydrous magnesium sulfate, and distilled. The residue, after removing the last trace of solvent i.v., weighed 1.26 g. (42%) and melted only one degree lower than pure *p*-nitroaniline. Identification was made by conversion to the acetyl and benzenesulfonyl derivatives and determination of mixed melting points with authentic samples.

The sodium hydroxide wash solution was neutralized to *p*H 7.5–8 and extracted four times with ether, yielding 0.1 g. of the dioxime.

p-Benzoquinonemonoxime benzenesulfonate. A modification of previously published procedures was used.[3,5,12] To 6.0 g. (0.049 mole) of nitrosophenol dissolved in 70 ml. of pyridine was added slowly 8.6 g. (0.049 mole) of benzenesulfonyl chloride, keeping the temperature of the reaction mixture under 25°. After the reaction mixture had been allowed to stand for 5 min., water was added slowly, with cooling, to precipitate the benzenesulfonate. The product was filtered, washed with 3*N* HCl and water until the odor of pyridine had been removed, and dried in a vacuum desiccator. The yield was 11.2 g. (94%) of fine, yellow needles, m.p. 130–131°, sufficiently pure for the subsequent steps. Pure material can be obtained by recrystallization from ether, m.p. 132.5–133°.[3]

p-Benzoquinonedioxime bis(benzenesulfonate)s. To 4 g. (0.029 mole) of *p*-benzoquinonedioxime dissolved in 45 ml. of pyridine was slowly added 14.8 g. (0.87 mole) of benzenesulfonyl chloride keeping the temperature of the reaction mixture under 55°. After 5 minutes of shaking, the reaction mixture was diluted with 150 ml. of water. The resulting precipitate was filtered, washed with 3*N* HCl and water, and dried in a vacuum desiccator. The yield was 11.95 g. (95%) of tan product which decomposed and sintered over the range 160–170°.

This product was recrystallized, with decolorization, from acetone to effect the primary separation of the high and low melting forms. The granules which formed, consisting mainly of the higher melting form, were filtered and dried, and purified by repeated crystallization from dry acetone. Sparkling, chunky crystals, m.p. 196–197° (dec.), or 203–204° (dec.) in a preheated bath.

Anal. Calcd. for $C_{18}H_{14}O_6N_2S_2$: C, 51.66; H, 3.37; N, 6.70; S, 15.33. Found: C, 52.15; H, 3.65; N, 6.85; S, 16.01.

To the filtrate from the primary separation was added enough water to precipitate the remainder of the derivative. By recrystallization of this product from carbon tetrachloride, the pure low melting form was obtained. Small white needles, m.p. 157–158° (dec.).

Anal. Calcd. for $C_{18}H_{14}O_6N_2S_2$: C, 51.66; H, 3.37; N, 6.70; S, 15.33. Found: C, 51.38; H, 3.43; N, 6.21; S, 15.43.

DECORAH, IOWA

---

(11) U. S. Patent **2,446,165**, *Chem. Abstr.*, **42**, 8213d (1948).

(12) E. Bornstein, *Ber.*, **29**, 1484 (1896).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY STATE UNIVERSITY OF IOWA]

Abnormal Beckmann Rearrangement of 9,10-Dihydro-9,10-(11-ketoethano)anthracene Oxime[1]

S. WAWZONEK AND J. V. HALLUM[2]

Received October 3, 1958

9,10-Dihydro-9,10-(11-ketoethano)anthracene oxime undergoes an abnormal Beckmann rearrangement when treated with either phosphorus pentachloride, benzenesulfonyl chloride and alkali, polyphosphoric acid, boron trifluoride, or hydrogen chloride. The first two reagents formed 9-anthranylacetonitrile while the last three gave 9-anthranylacetamide. The structures of these two products were demonstrated by synthesis.

In previous work on the determination of the importance of three dimensional structures in the analgetic behavior of compounds, 9,10-dihydro-9,10-(11-aminoethano)anthracenes were synthesized and found to be inactive as analgetics.[3]

Attempts to modify this three dimensional structural feature by including the nitrogen in the bridge is described in the present work. A Beckmann rearrangement of 9,10-dihydro-9,10-(11-ketoethano)-anthracene oxime (I) was tried with phosphorus pentachloride and found to yield 9-anthranylacetonitrile (II). This reaction is analogous to the second order Beckmann rearrangement observed with the oximes of aldehydes, pivalophenone[4] and other tertiary ketones[5] under similar conditions.

Since benzenesulfonyl chloride and alkali and hydrogen chloride in acetic acid often give a normal rearrangement with some of these examples,[4] these reagents were also tried on the oxime I. The first of these gave the nitrile II while the

---

(1) Abstracted in part from the Ph.D. thesis of J. V. Hallum, August 1952.

(2) Public Health Research Fellow of the National Institutes of Health, 1951–52.

(3) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

(4) R. F. Brown, N. M. van Gulick, and G. H. Schmid, *J. Am. Chem. Soc.*, **77**, 1094 (1955).

(5) R. E. Lyle and G. G. Lyle, *J. Org. Chem.*, **18**, 1058 (1953).