

assigned by Fittig and Strom to their compound. This formulation was rejected by Burdick and Adkins because the resistance to hydrolysis of the compound did not seem in harmony with an acetal type of structure.

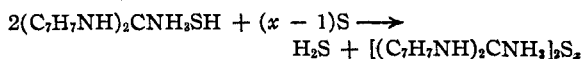
MADISON, WISCONSIN RECEIVED SEPTEMBER 24, 1934

Diphenyl- and Di-*o*-tolylguanidinium Polyselenides

BY R. L. McCLEARY AND W. CONARD FERNELIUS

Work conducted in this Laboratory¹ has proved the existence of diphenyl-, di-*o*-tolyl- and di-*p*-tolylguanidinium polysulfides. Furthermore, it has been possible to isolate the hydrosulfide of diphenylguanidine.²

These polysulfides were prepared by passing hydrogen sulfide through a suspension of the substituted guanidine in 95% ethanol until all the base had gone into solution as a hydrosulfide. After warming the solutions to about 60°, purified sulfur was added until no more went into solution. Hydrogen sulfide was evolved during the reactions as may be shown by the equation



Upon standing and allowing to cool, the red supernatant liquids soon deposited brick red micro-crystalline materials which proved to be the heptasulfides.

Preparation of Diphenylguanidinium Polyselenide.—Ethanol was freed of air by boiling and cooling in a stream of nitrogen. Hydrogen selenide, generated by the hydrolysis of aluminum selenide, was passed through a drying tower and into a suspension of diphenylguanidine in the above ethanol. A solution, slightly orange in color, resulted. On adding powdered selenium, the solution became dark red. When selenium was no longer dissolved, the solution was decanted from the excess selenium. After standing for some time (a much longer period than for the guanidinium polysulfides) a fine crystalline material separated from the solution which when dry exhibited a dark gray-purple color: decomposition range 152–156°.

Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_6\text{Se}_4$: Se, 42.7; N, 11.3. Found: Se,³ 42.9, 40.7; N, 11.4, 11.3.

Preparation of Di-*o*-tolylguanidinium Polyselenide.—Identical results were obtained substituting di-*o*-tolylguanidine for the diphenyl compound in the above operations; decomposition point of the tetraselenide 170–174°.

Anal. Calcd. for $\text{C}_{30}\text{H}_{26}\text{N}_6\text{Se}_4$: Se, 39.7; N, 10.5. Found: Se, 39.5, 40.2; N, 10.4, 10.2.

(1) M. C. Reed (with C. E. Boord), Dissertation, The Ohio State University, 1925. D. E. Strain (with C. E. Boord), Dissertation, The Ohio State University, 1927.

(2) M. Achterhof, R. F. Conaway and C. E. Boord, *THIS JOURNAL*, **53**, 2682–2688 (1931).

(3) Determined by the method of E. H. Shaw, Jr., and E. B. Reid, *THIS JOURNAL*, **49**, 2330–2334 (1927).

These tetraselenides are decomposed with extreme ease by dilute acids to yield amorphous black selenium and hydrogen selenide. A portion of the latter seems to be either decomposed or oxidized at the moment of its liberation.

Anal. On treatment with dilute HCl, 0.4344 g. of diphenylguanidinium tetraselenide deposited 0.1766 g. or 40.8% Se. Calcd.: 3 Se, 32.1; 4 Se, 42.7. H_2Se identified by its odor. Neutralization of the filtrate gave crystals of diphenylguanidine, m. p. 148°.

Attempts were made to isolate an amine hydroselenide in a system closed to the air but were unsuccessful because of the continual decomposition of the hydrogen selenide.

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α -Oximino and α -Amino Derivatives of *o*-Hydroxypropiophenone

BY HAROLD L. MASON

In 1931 Hartung, Munch, Miller and Crossley¹ described the preparation of a series of phenolic arylisonitroso ketones. They did not succeed, however, in obtaining *o*-hydroxyphenyl- α -oximinoethyl ketone because the ortho phenolic group interfered in some way. This compound has now been prepared through the intermediacy of *o*-benzoyloxypropiophenone and *o*-benzoyloxyphenyl α -oximinoethyl ketone. The latter has been reduced to the corresponding amine. It should be easily possible by means of obvious reactions to convert this ketone amine to *o*-hydroxyphenylpropanolamine. The investigation has not been carried that far, and, since it cannot be continued, the results are presented at this time.

Experimental

***o*-Benzoyloxypropiophenone.**—This was prepared from *o*-hydroxypropiophenone and benzoyl chloride by the Schotten-Baumann reaction. After recrystallization from petroleum ether it melted at 58–59°.

***o*-Benzoyloxyphenyl α -Oximinoethyl Ketone.**—The nitrosation of *o*-benzoyloxypropiophenone was carried out as described by Hartung¹ and his associates. Sixty grams of *o*-benzoyloxypropiophenone partially dissolved in 150 cc. of ether was treated with 24.6 g. of butyl nitrite while bubbling in hydrogen chloride. After completion of the reaction the ether was removed under reduced pressure. The partially crystalline residue was dissolved in 35 cc. of benzene and petroleum ether added slowly with rapid stirring. The product crystallized slowly. After drying at 60° it weighed 49 g., a yield of 73%. It melted at 100–101°.

(1) Hartung, Munch, Miller and Crossley, *THIS JOURNAL*, **53**, 4149 (1931).

Anal. Calcd. for $C_{16}H_{13}O_4N$: C, 67.82; H, 4.63. Found: C, 67.54; H, 4.88.

***o*-Hydroxyphenyl α -Oximinoethyl Ketone.**—*o*-Benzoyloxyphenyl α -oximinoethyl ketone (8.4 g.) in alcoholic solution was treated with 15 cc. of 5 *N* sodium hydroxide solution. After fifteen minutes the solution was diluted with water and made just acid to litmus with acetic acid. The yellow oil which separated was dissolved in ether. The ether solution was washed with a solution of sodium carbonate and dried over sodium sulfate. After removal of the ether the partially crystalline residue was dissolved in hot petroleum ether. The large yellow plates which separated on cooling melted at 85–88°. Another recrystallization did not change the melting point. Ferric chloride produced a deep red color in alcoholic solution.

Anal. Calcd. for $C_{16}H_{13}O_3N$: C, 60.31; H, 5.07. Found: C, 60.19; H, 5.23.

***o*-Benzoyloxyphenyl α -Aminoethyl Ketone.**—The oximino ketone was reduced catalytically in absolute alcohol solution following the conditions of Hartung and Munch.² The uptake of hydrogen did not stop completely when two moles had been absorbed but the rate fell off quite sharply at that point. However, much of the hydrogen was used up in side reactions since the yield of amine was only 30%. A large proportion of the oximino ketone was recovered unchanged. This was accompanied by a small amount of oil which was not investigated.

After removal of the catalyst the solution was evaporated under reduced pressure to about 25 cc. and an equal vol-

ume of dry ether added. The hydrochloride of the amine separated as long interlacing needles which decomposed at about 180° without melting. For recrystallization it was dissolved in hot alcohol containing 1 cc. of concd. hydrochloric acid. After filtration acetone was added slowly. The crystals which separated apparently contained one-half molecule of water. However, loss of weight at 120° was negligible. After two hours at 125–130° there was some loss of weight but there was also evidence of some decomposition.

Anal. Calcd. for $C_{16}H_{13}O_3NCl$: C, 62.83; H, 5.82. Calcd. for $C_{16}H_{13}O_3NCl \cdot 0.5H_2O$: C, 61.03; H, 5.45. Found: C, 61.00, 61.35; H, 5.50, 5.48.

The free base was prepared by neutralization of an aqueous solution of the hydrochloride with sodium carbonate. It precipitated as fine needles. After recrystallization from petroleum ether they melted at 112–114°. They reduced Fehling's solution.

Anal. Calcd. for $C_{16}H_{13}O_3N$: C, 71.34; H, 5.62. Found: C, 71.32; H, 5.75.

Summary

o-Benzoyloxy α -oximinoethyl ketone has been prepared. It has been converted into *o*-hydroxyphenyl α -oximinoethyl ketone by hydrolysis and into *o*-benzoyloxyphenyl α -aminoethyl ketone by catalytic hydrogenation.

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(2) Hartung and Munch, *THIS JOURNAL*, **61**, 2262 (1929).

COMMUNICATIONS TO THE EDITOR

A BENZALDEHYDE ELECTRODE

Sir:

In "the difficult alkaline range" of *pH* we have substituted benzaldehyde for quinhydrone in a regular quinhydrone *pH* determination apparatus, and, using a saturated calomel electrode as reference, have made reproducible determinations between *pH* 7 and 13.64. Checked against a hydrogen electrode, the deviations in *pH* units in a large number of measurements were: 0.00–0.09 unit, 44.36%; 0.10–0.19 unit, 33.12%; 0.20–0.29 unit, 14.57%; 0.30–0.39 unit, 5.30%; 0.40–0.49 unit, 2.65%; above 0.50 unit, 0.00%. Comparable to colorimetric readings, therefore, the benzaldehyde electrode gave accuracy within 0.2 *pH* in 77.48% of the determinations.

The determinations were carried out in 50-cc. Pyrex beakers, with 40 cc. of the solution and 0.4

cc. of benzaldehyde mixed by a stirrer at 1200 r. p. m. The electrode was a 10-cm. coil of platinum wire. The connection was through a salt bridge into saturated potassium chloride, into which the calomel electrode tip dips.

From the data a master curve has been plotted, smoothed mathematically, which presents potentials as ordinates against *pH* values as abscissas. The coefficient of correlation between the *pH* values obtained with the benzaldehyde electrode and with the hydrogen electrode between *pH* 7 and 14 is 0.996 ± 0.0006 . The most reproducible region is between *pH* 9 and 14.

A linear relationship was found to exist between the common logarithm of the absolute potential of the benzaldehyde electrode (found by adding 0.5266, the so-called absolute potential of the saturated calomel electrode, to the observed po-