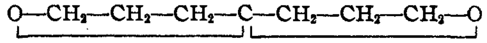

assigned by Fittig and Strom to their compound. This formulation was rejected by Burdick and Adkins because the resistance to hydrolysis of the compound did not seem in harmony with an acetal type of structure.

MADISON, WISCONSIN RECEIVED SEPTEMBER 24, 1934

Diphenyl- and Di-*o*-tolylguanidinium Polyselenides

BY R. L. MCCLEARY AND W. CONARD FERNELIUS

Work conducted in this Laboratory[1] 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

$$2(C_7H_7NH)_2CNH_3SH + (x - 1)S \longrightarrow H_2S + [(C_7H_7NH)_2CNH_3]_2S_x$$

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 $C_{26}H_{28}N_6Se_4$: 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 $C_{30}H_{36}N_6Se_4$: Se, 39.7; N, 10.5. Found: Se, 39.5, 40.2; N, 10.4, 10.2.

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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[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. E. Reid, THIS JOURNAL, **49**, 2330–2334 (1927).

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

BY HAROLD L. MASON

In 1931 Hartung, Munch, Miller and Crossley[1] 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 Hartung[1] 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°.

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