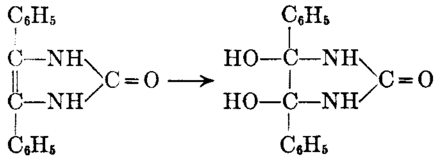
The Oxidation of 4,5-Diphenyl-2-imidazolone

W. R. DUNNAVANT

Received July 19, 1956

The sole practical method reported[1] for the oxidation of 4,5-diphenyl-2-imidazolone (I) to 4,5-diphenyl - 4,5 - dihydroxy - 2 - imidazolone (II) utilizes concentrated nitric acid as the oxidant.



I II

Numerous failures to duplicate this method indicated the lack of specific detail in the description of the synthetic method. It is essential that the nitric acid be cooled to 0° before addition to a slurry of I in glacial acetic acid at the same temperature. Addition of the acid at room temperature results in benzil or N,N′-dibenzoyl urea as the sole products isolable.

Cursory attempts to hydroxylate I using several catalyzed hydrogen peroxide reagents or performic acid resulted only in N,N′-dibenzoyl urea, benzil, or benzoic acid.

In view that the rather unusual nitric acid hydroxylation method may be applicable to other carbon-carbon double bonds with adjacent amide linkages where the customary hydroxylating reagents may fail it is deemed desirable to report the clarified reaction procedure.

EXPERIMENTAL[2]

4,5-Diphenyl-4,5-dihydroxy-2-imidazolone. A suspension of I[3] (2 g.) in 30 ml. of glacial acetic acid was chilled to a thick slurry with rapid stirring in an ice-bath at 0°. Concentrated nitric acid (2 ml.) was chilled to the same temperature and then was added dropwise to the slurry. As soon as a clear green solution formed 50 ml. of water was added in small portions and the mixture was stirred rapidly for 30 minutes. A fine precipitate formed which was filtered, dried, and then stirred twice with 30-ml. portions of a 1:3 ethanol–ether mixture to remove impurities. The yield was 0.99 g. (43%) of very small white crystals of II. After recrystallization from ethanol the white crystals turned yellow at 155° and partially fused with decomposition at 158–161° when heated at 6° per minute.[4] The product showed hydroxyl absorption at 2.95 μ in the infrared and rearranged to 5,5-diphenyl hydantoin upon refluxing for two hours with ethanolic potassium hydroxide.

Anal. Calc'd for $C_{15}H_{14}N_2O_3$: C, 66.65; H, 5.22; H, 10.36. Found: C, 66.79; H, 5.21; N, 10.22.

CHEMISTRY RESEARCH BRANCH
AERONAUTICAL RESEARCH LABORATORY
DIRECTORATE OF RESEARCH
WRIGHT AIR DEVELOPMENT CENTER
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

---

[1] Biltz, *Ann.*, **368**, 173 (1907).

[2] M.p. is uncorrected and was obtained on a Fisher-Johns melting-point block. The microanalysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

[3] Corson and Freeborn, *Org. Syntheses*, Coll. Vol. 2, 231 (1950).

[4] Slow heating, *i.e.* 1–2° per minute resulted in yellowing at 155°, but no apparent fusion occurred.

Magnesium Bromide Catalysis in the Lithium Borohydride Reduction of Substituted Styrene Oxides

GENE J. PARK AND RICHARD FUCHS

Received July 19, 1956

Previous studies[1,2] on the reduction of substituted sytrene oxides with lithium borohydride demonstrated that electron-donating substituents favor the reaction at the benzyl carbon atom with formation of primary alcohols, and electron withdrawing substituents usually favor the formation secondary alcohols. A plot of log % primary alcohol *vs. sigma* is a straight line,[2] with the exception of the point representing *p*-nitrostyrene oxide.

All of the oxides are believed to react by S_N2 mechanisms, but a somewhat different transition state is probably involved in the reaction of *p*-nitrostyrene oxide. The negative *rho* value for the reaction suggests that the electron density at the benzyl carbon atom is lower in the transition state than in the initial molecule, a condition which is stabilized by electron-donating substituents. On the other hand, the *p*-nitrostyrene oxide molecule is somewhat electron-deficient at the benzyl carbon atom, facilitating C–H bond formation and inhibiting C–O bond rupture. In attaining the transition state there is an increase in electron density at the benzyl carbon atom. The extreme examples of such a mechanism involve preliminary addition of the nucleophile, and may occur with silicon halides, aryl halides, and, in some cases, acyl halides. The coordination number of the central atom is increased before halide ion departs.

From this transition state—substituent effect relationship one would predict that any factor further decreasing the electron density in the transition state should increase the reactivity of the benzyl carbon atom of *p*-methylstyrene oxide and decrease the reactivity of the benzyl carbon atom of *p*-nitrostyrene oxide. Experimentally, this has been realized by adding magnesium bromide as an electrophile. The opposite effect should be observed by increasing the nucleophilicity (or, pos-

---

[1] Fuchs and VanderWerf, *J. Am. Chem. Soc.*, **76**, 1631 (1954).

[2] Fuchs, *J. Am. Chem. Soc.*, **78**, 5612 (1956).