On the Reduction of Quinoxaline

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Received February 11, 1963

Quinoxaline may be converted to 1,2,3,4-tetrahydroquinoxaline, m.p. 97°, by the action of sodium in boiling ethanol.[1] The reaction is characterized by a transitory green color of the reaction mixture and mediocre yields are obtained. 1,2- or 1,4-Dihydroquinoxaline have not been isolated by this method. Treatment with lithium aluminum hydride or catalytic hydrogenation also yield the tetrahydro compound from quinoxaline.

A different reaction product was obtained in this laboratory when the quinoxaline anion was prepared first by treating quinoxaline dissolved in tetrahydrofuran with sodium, followed by the addition of ethanol to this solution. The sodium–quinoxaline solution had a deep purple color. Addition of absolute ethanol to this solution turned its color light green. Further addition of water precipitated a light tan solid (I), m.p. 158–159°, after purification. Addition of water directly to the sodium–quinoxaline solution, however, yielded the starting material.

We have found compound I to be the thus far unknown 1,4-dihydroquinoxaline. The reaction leading to this product appears to be similar to that of sodium–naphthalene with water, alcohols, or practically any source of acidic hydrogen,[2] yielding 1,4-dihydronaphthalene. On the other hand, sodium–quinoline was found not to yield a dihydro compound in this laboratory, which perhaps may be ascribed to the instability of these compounds.

Chemical analysis and molecular weight determination of compound I indicated a dihydroquinoxaline $C_8H_8N_2$. An n.m.r. spectrum could not be obtained because of insufficient solubility in suitable solvents at room temperature.[3] A comparison of the infrared spectra of quinoxaline, compound I, and 1,2,3,4-tetrahydroquinoxaline showed the presence of a strong absorption maximum at about 1600 cm.$^{-1}$ in the spectra of compound I and of 1,2,3,4-tetrahydroquinoxaline, which was absent in the spectrum of quinoxaline. Furthermore, the spectra of compound I and 1,2,3,4-tetrahydroquinoxaline exhibited strong absorption maxima at about 750 cm.$^{-1}$, due to out-of-plane CH bending of the *o*-substituted phenyl ring, and at about 3250 cm.$^{-1}$, due to NH stretching. The same two spectra showed identical peaks between 1300 and 2500 cm.$^{-1}$, which indicated the absence of —C=N— in compound I, and meant that the maximum at about 1600 cm.$^{-1}$ was due to the phenyl ring in compound I and in 1,2,3,4-tetrahydroquinoxaline. All spectra were determined using potassium bromide pellets.

An active hydrogen analysis of compound I employing methylmagnesium iodide showed the presence, respectively, of 1.32 and 1.38% active hydrogen, corresponding to the presence, respectively, of 1.75 and 1.82 atoms of active hydrogen per molecule of compound I. The evidence warrants the conclusion that compound I is 1,4-dihydroquinoxaline and not 1,2-dihydroquinoxaline, since the former contains two active hydrogens and the latter only one.

The conclusion that compound I was 1,4-dihydroquinoxaline was further confirmed by the fact that it did not fluoresce in ethanol solution. This is a well known property of 1,2-dihydroquinoxalines,[4] but not of 1,4-dihydroquinoxalines.

Treatment of compound I with lithium aluminum hydride yielded 1,2,3,4-tetrahydroquinoxaline under mild conditions. Quinoxaline itself yielded 90% of the tetrahydro compound under similar conditions.[5] The reduction of compound I seems to provide one of the few examples of the reduction of a carbon–carbon double bond by lithium aluminum hydride.

Experimental[6]

Sodium–Quinoxaline.—Quinoxaline, 5.7 g. (43 mmoles), was dissolved in anhydrous tetrahydrofuran, 75 ml., under a nitrogen atmosphere, to which sodium, 2.0 g. (87 mmoles), was added. The initially colorless solution turned deep purple.

Compound I.—1,4-Dihydroquinoxaline was prepared by the addition of anhydrous ethanol, 40 ml., to the solution of sodium–quinoxaline described before, at room temperature. After about 10 min., the light green alcoholic solution was added to water, 1 l., and a light tan solid precipitated, which was collected and washed with petroleum ether, m.p. 158–159°; yield, 1.5 g. (26%).

Pertinent infrared bands: NH stretching, 3240 cm.$^{-1}$; CH bending, 747 cm.$^{-1}$; phenyl nucleus, 1605 cm.$^{-1}$. Spectra were determined using potassium bromide pellets.

Anal. Calcd. for $C_8H_8N_2$: C, 72.69; H, 6.10; N, 21.18; mol. wt., 132. Found: C, 72.38; H, 5.92; N, 20.92; mol. wt., 117 (Rast method).

Anal.[7] Calcd. for two active hydrogen atoms per molecule $C_8H_8N_2$: H, 1.52. Found: H, 1.32 and 1.38.

1,2,3,4-Tetrahydroquinoxaline.—This compound was prepared (a) from quinoxaline and (b) from 1,4-dihydroquinoxaline (compound I).

(a) Treatment of quinoxaline with sodium and boiling ethanol yielded the tetrahydro compound in a 20% yield.[1] (b) Treatment of 1,4-dihydroquinoxaline with lithium aluminum hydride in ether[5] yielded the tetrahydro compound in a 43% yield. Compound I, 0.8 g. (6 mmoles), was added to anhydrous ether, 40 ml., to which was then added lithium aluminum hydride, 1.5 g. (40 mmoles), at room temperature. The mixture was allowed to react for 24 hr. Saturated ammonium chloride solution was then added slowly to the ether mixture, until all excess lithium aluminum hydride was destroyed. The mixture was filtered and the solvent evaporated. The residue was recrystallized three times from a benzene–petroleum ether mixture; yield, 0.3 g. (43%); m.p. 95.5–97° (lit.[5,1] m.p. 91–97.5°).

Pertinent infrared bands: NH stretching, 3220 cm.$^{-1}$; CH bending, 745 cm.$^{-1}$; phenyl nucleus, 1595 cm.$^{-1}$. Spectra were determined using potassium bromide pellets.

Acknowledgment.—We are indebted to the Greater New Orleans Cancer Association and to the Undergraduate Research Participation Program of the National Science Foundation, each of which supported part of this investigation.

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(5) F. Bohlmann, *Ber.*, **85**, 390 (1952).

(6) All melting points are uncorrected. Spectra were recorded with a Beckman IR-5. Microanalysis were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(7) Determined by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Mulheim, West Germany.