Notes A department for short papers of immediate interest.

Quinoxaline-2-Thiols

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Received October 24, 1955

The only representative of the class of quinoxaline-2-thiols was recently reported by Wolf, Wilson, Jr., and Tishler.[3]

This paper presents the preparation of quinoxaline-2,3-dithiol, an unusually sensitive reagent for nickel. The dithiol was prepared by treating 2,3-dichloroquinoxaline with thiourea and hydrolyzing the isothiouronium salt. This compound was also made by refluxing a mixture of 2,3-dihydroxyquinoxaline and phosphorus pentasulfide in dry pyridine.

Also described is the preparation of 3-alkylquinoxaline-2-thiols. These compounds were prepared directly by treating the corresponding chloroquinoxalines with thiourea in absolute alcohol. The intermediate isothiouronium salts did not precipitate, and the desired thiols crystallized on cooling.

All of these thiols were characterized by converting them to mercapto ethers.

EXPERIMENTAL[4]

Quinoxaline-2,3-dithiol. (*a*) *From 2,3-dichloroquinoxaline.* A solution of 4 g. (0.02 mole) of 2,3-dichloroquinoxaline[5] and 8 g. (0.105 mole) of thiourea in 100 ml. of absolute alcohol was refluxed for two hours. The solution was concentrated to a small volume, diluted with 250 ml. of water, made alkaline by the addition of 25 g. sodium hydroxide, and then refluxed for one-half hour. On acidifying with acetic acid, a brownish-orange product formed which was separated by filtration, washed with water and dried. The yield was 3.76 g. or 96.4%.

The dithiol could not be recrystallized from any solvent tried, but was purified for analysis by repeated dissolving in alkali and reprecipitation by acetic acid. Prolonged heating in alkaline solution appeared to cause some oxidation and lightening of color. A characteristic behavior was shown on heating. Between 230–250° the color of the compound started to change to chrome yellow; the change was completed by 280°. Decomposition began at 290–295°, with partial fusion, at which point the substance turned greenish-gray.

Anal. Calc'd for $C_8H_6N_2S_2$: C, 49.48; H, 3.09. Found: C, 48.89; H, 3.27.

(*b*) *From 2,3-dihydroxyquinoxaline.* A dry pyridine solution of 7.3 g. (0.045 mole) 2,3-dihydroxyquinoxaline[6] and 33 g. (excess) phosphorus pentasulfide was refluxed for two hours following the procedure of Elion and Hitchings.[7] After the black solution cooled, the pyridine was removed by concentrating under reduced pressure. The residue was taken up with 100 ml. of water, heated on a steam-bath for one hour, cooled, and then made alkaline with 100 ml. of concentrated ammonium hydroxide. The mixture was chilled overnight, then filtered, and the filtrate was acidified with acetic acid to *p*H 5. The precipitate was removed by filtration, washed with water, and redissolved with ammonium hydroxide. Again the filtrate was acidified to *p*H 5, and the solid was filtered, washed, and dried.

The yield of reddish-brown material was 5.4 g. (61.9%). The melting point was previously described.

Anal. Calc'd for $C_8H_6N_2S_2$: N, 14.43. Found: N, 14.20.

The quinoxaline-2,3-dithiol forms chelates or salts of varying color with a number of transition metal ions. With the amino-nickel cation at very high dilution, a clear pink solution is formed. This reaction is being investigated as a new method for the colorimetric determination of nickel.

3-Methylquinoxaline-2-thiol. A solution containing 3.2 g. (0.018 mole) of 2-chloro-3-methylquinoxaline,[8] and 6 g. (0.079 mole) of thiourea in 50 ml. of absolute alcohol was refluxed for two hours and then was concentrated to about 15 ml. On cooling, the thiol crystallized and was recrystallized from acetone, m.p. 240–245° with dec.; 2.95 g. (93.6%).

Anal. Calc'd for $C_9H_8N_2S$: C, 61.36; H, 4.55. Found: C, 61.60; H, 4.73.

3-Isopropylquinoxaline-2-thiol. The 2-chloro-3-isopropylquinoxaline was made similar to the method of L'Italien and Banks[8] in 85% yield. The m.p. was 61°.

Anal. Calc'd for $C_{11}H_{11}ClN_2$: C, 63.92; H, 5.33. Found: C, 64.01; H, 5.45.

Following the procedure outlined above, the chloro compound was converted to 3-isopropylquinoxaline-2-thiol in 95% yield, m.p. sintered 195°; dec. 215–225°.

Anal. Calc'd for $C_{11}H_{12}N_2S$: C, 64.71; H, 5.88. Found: C, 65.16; H, 6.02.

DERIVATIVES

The 3-alkylquinoxaline-2-thiols were converted to the respective thiol ethers by mixing 0.8 g. of the thiol with 5 ml. of methyl iodide in 50 ml. absolute alcohol and allowing the mixture to remain at room temperature for 2$^1/_2$ weeks. The solution was evaporated to dryness and the black residue was extracted repeatedly with petroleum ether. The combined extracts were treated with decolorizing carbon and again were evaporated to dryness. The remaining oil was dissolved in acetone-water. On cooling, a solid formed which was recrystallized several times from acetone-water.

For *3-(methylthio)-2-methylquinoxaline* the yield was 78.5% and the m.p. was 51.5–53°.

Anal. Calc'd for $C_{10}H_{10}N_2S$: C, 63.16; H, 5.26. Found: C, 63.53; H, 5.62.

For *2-(methylthio)-3-isopropylquinoxaline* the yield was 84.2% with a m.p. of 66–67°.

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(3) Wolf, Wilson, Jr., and Tishler, *J. Am Chem. Soc.*, **76**, 2266 (1954).

(4) Microanalyses are by Microchemical Specialties, Berkeley, California.

(5) Hinsberg and Pollak, *Ber.*, **29**, 784 (1896).

(6) Newbold and Spring, *J. Chem. Soc.*, 519 (1948).

(7) Elion and Hitchings, *J. Am. Chem. Soc.*, **77**, 1676 (1955).

(8) L'Italien and Banks, *J. Am. Chem. Soc.*, **73**, 3246 (1951).

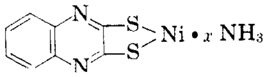
Anal. Calc'd. for $C_{12}H_{14}N_2S$: C, 66.06; H, 6.42. Found: C, 66.20; H, 6.43.

Quinoxaline-2,3-dithiol was ethylated by digesting 1 g. of the thiol with 3 g. of sodium hydroxide in 50 ml. of 95% alcohol, then adding 5 ml. of ethyl iodide and refluxing for $1^1/_2$ hours. The solvents were evaporated and the material was treated as described above. The yield of white product, which melted at 48–50°, was 84.6%.

The *2,3-di-(ethylthio)quinoxaline* was also prepared from 2,3-dichloroquinoxaline and sodium ethyl mercaptide. To an alcohol solution of 5 ml. (0.068 mole) of ethyl mercaptan was first added 0.6 g. (0.026 mole) of sodium and then 1.7 g. (0.0085 mole) of the dichloroquinoxaline. The solution was refluxed for 5 hours, cooled, diluted with water, and the mixture was distilled until most of the alcohol was removed. On cooling, the remaining oil was extracted with ether and the ether solution was evaporated. The residue was extracted with petroleum ether, decolorized with charcoal, and evaporated. The oil crystallized, forming 1.72 g. of product or 80.5%. This substance, recrystallized several times from acetone-water, had m.p. 50–51°. The mixture m.p. was 49–50°.

Anal. Calc'd for $C_{12}H_{14}N_2S_2$: C, 57.60; H, 5.60; S, 25.60. Found: C, 57.78; H, 5.76; S, 25.38.

Nickel derivative. The addition of an ammoniacal nickel solution to the yellow solution of quinoxaline 2,3-dithiol in concentrated ammonium hydroxide gave a dark red liquid. Concentrated solutions formed a crystalline precipitate at once. This substance was washed with NH_4OH and air-dried. If the non-volatile residue from combustion analysis was assumed to be Ni_3O_4, then the formula of the nickel complex would probably be:



Anal. Calc'd for hexamine $C_8H_{22}N_8NiS_2$: C, 27.22; H, 6.24; Ni, 16.64; Calc'd for tetramine $C_8H_{16}N_6NiS_2$: C, 30.11; H, 5.02; Ni, 18.41. Found: C, 28.09; H, 4.57; Ni, 18.1.

When the crystalline Ni derivative was digested with hot water, it hydrolyzed to an amorphous *magenta*-colored flocculent substance of great coloring power. This is probably a *lake*, since it showed a high Ni content and little organic matter.

Analysis of the air-dried product: C, 3.81; H, 2.74; Ni, 55.56.

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The Synthesis and Some Reactions of 9-Fluorenyl Nitrate[1]

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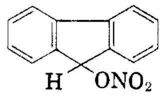
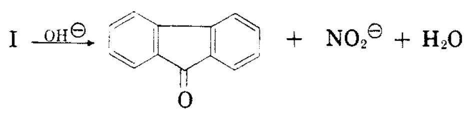
Received November 17, 1955

Interest in the hydrolytic and thermal decomposition of nitrate esters has led recently to the synthesis of benzhydryl nitrate,[2,3,4] triphenylmethyl nitrate,[3,4,5] and tri-(*p*-nitrophenyl)methyl nitrate.[6] Of these the first two are extremely sensitive towards hydrolysis and are very difficult to obtain in a pure form. It has now been found that 9-fluorenyl nitrate (I), a structural analog of benzhydryl nitrate, may be prepared easily and that it is stable to hydrolysis and decomposition during storage. It was prepared by the action of silver nitrate on 9-bromofluorene in acetonitrile,[7] and is a white crystalline solid which can be purified readily by crystallization.



I

A cursory examination of the reactions of 9-fluorenyl nitrate with acid and base has been made. When the compound was dissolved in methanolic potassium hydroxide, a deep yellow color immediately appeared and crystals of fluorenone (II) were deposited; no fluorenol was found. Thus this nitrate ester appears to undergo alkaline hydrolysis exclusively by the α-hydrogen elimination process[8,2] yielding the ketone and nitrite ion. Other nitrate esters which hydrolyze in base exclusively by this process are trichloroethyl nitrate,[9] α-nitratoketones,[10] and the nitrobenzyl nitrates.[2] These results indicate that the acidity of the α-hydrogen atom may be the determining factor in the α-elimination process thus suggesting that the transition state for this process is close to reactants. However, it still has not been determined whether the process is concerted or involves a discrete carbanion intermediate and thus the contribution of the carbonyl forming reaction to the transition state is unknown.[11]



II

When 9-fluorenyl nitrate was dissolved in 95% sulfuric acid, a deep blue green color appeared. When the sulfuric acid solution of the nitrate ester was poured into water, 9-fluorenol was formed. It thus appears that this nitrate ester is solvolyzed to the 9-fluorenyl carbonium ion (blue-green color) in strong acid. The same color was generated when 9-fluorenol was dissolved in sulfuric acid.

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] Baker and Heggs, *J. Chem. Soc.*, 616 (1955).

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(8) Baker and Easty, *J. Chem. Soc.*, 1207 (1952).

(9) Emmons, McCallum, and Freeman, *J. Org. Chem.*, **19**, 1472 (1954).

(10) Emmons and Freeman, *J. Am. Chem. Soc.*, **77**, 4415 (1955).

(11) For a more detailed consideration of the α-elimination reaction, see ref. 2, p. 623.