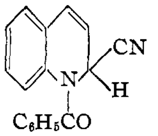
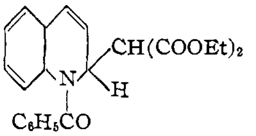
quinaldinonitrile (I). This crystalline compound yields quinaldinic acid and benzaldehyde on acid hydrolysis.



I

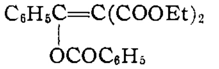


II

The reaction may be used as a method of reducing acyl halides to aldehydes, especially in the aromatic series.[3] Aliphatic acyl halides can be reduced similarly if anhydrous conditions are employed.[4]

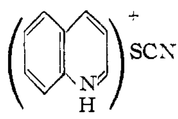
The present investigation was undertaken to determine whether this reaction could be extended by the use of salts other than potassium cyanide. Potassium thiocyanate and ethyl sodiomalonate were selected for preliminary study.

The reaction of benzoyl chloride with quinoline and ethyl sodiomalonate did not yield the desired 1,2-dihydroquinoline derivative (II), since most of the quinoline was recovered. It is known[5] that when benzoyl chloride and sodiomalonic ester react in the absence of quinoline, the products obtained are benzoylmalonic ester and a dibenzoyl derivative, III. These products seemed to be formed in the present investigation as judged by their behavior toward hydrolysis.



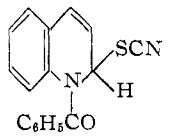
$$\underset{\displaystyle OCOC_6H_5}{C_6H_5C}{=}C(COOEt)_2$$

III

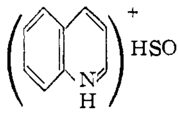


IV

The reaction of benzoyl chloride with quinoline and potassium thiocyanate in water gave a good yield of a crystalline product, but it proved to be quinolinium thiocyanate (IV), not V.



V



VI

Oxidation of IV with nitric acid produced quinolinium hydrogen sulfate (VI).

Experimental

Reaction of Benzoyl Chloride with Quinoline and Ethyl Sodiomalonate.—A mixture of 0.28 mole each of quinoline, benzoyl chloride and ethyl sodiomalonate in 215 ml. of benzene was refluxed for one hour. Solvent was removed and 200 g. of ice water was added to the residue. The layers were separated. The non-aqueous layer was washed with two 100-ml. portions of water, dried (Na_2SO_4) and distilled.

Fraction	B. p., °C.	Pressure, mm.	Weight, g.
a	43–83	25	8.5
b	80–100	15	44
c	70–130	2	16.5
d	Residue	..	25

The alkaline hydrolysis of 2 g. of fraction c yielded 0.7 g. of benzoic acid, m.p. 122–123°. Acid hydrolysis of residue d gave rise to a ketone; 2,4-dinitrophenylhydrazone, m.p. 239–240° (uncor.). The reported m.p. of acetophenone 2,4-dinitrophenylhydrazone is 249° (cor.). Fractions a and b were combined and extracted with two 50-ml. portions of 6 *N* hydrochloric acid. Eighteen grams of material was insoluble. The acid solution was made alkaline and extracted with 100 ml. of ether. Evaporation of the ether left 31 g. of quinoline, b.p. 109° at 14 mm. The reactions of fraction c with alkali and of the residue (d) with acid are similar to those reported[5] for benzoylmalonic ester and the dibenzoyl derivative (III), respectively.

Quinolinium Thiocyanate (IV).—To a stirred and cooled mixture of 63 g. of redistilled quinoline and 156 g. of potassium thiocyanate in 600 ml. of water, there was added 148 g. of benzoyl chloride in seven minutes. After one hour of stirring, most of the aqueous solution was removed by decantation and 70 ml. of ether was added to the residue. The insoluble tan solid was collected by filtration, washed with two 100-ml. portions of ether, and dried at 50°. A yield of 71 g. (77%) of quinolinium thiocyanate was obtained. This material was recrystallized from 200 ml. of absolute alcohol yielding 60 g. of light yellow material melting at 140–142°. A sample for analysis was recrystallized from methanol; m.p. 141–141.5°.

Anal. (by M. Ledyard) Calcd. for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; neut. equiv., 188.2. Found: C, 64.04; H, 4.50; neut. equiv., 186.4, 191.2, 189.4.

A qualitative analysis (sodium fusion) indicated the presence of sulfur. No ash was obtained on ignition. A deep red color was produced immediately upon the addition of a few drops of ferric chloride solution to a hot aqueous solution of the product.

Quinolinium Hydrogen Sulfate (VI).—Fourteen grams of quinolinium thiocyanate was added in small portions to 25 ml. of concentrated nitric acid. A vigorous reaction occurred on each addition. The mixture was heated on the steam-bath for one hour and then was evaporated to dryness. The residue was heated with 75 ml. of absolute alcohol, and the mixture was filtered to remove a small amount of insoluble material. The filtrate was cooled. The precipitated solid was collected by filtration and recrystallized five times from absolute alcohol. There was obtained 2.5 g. of material melting at 162–164°. An additional 6.5 g. of material, m.p. 162–166°, was obtained by concentration of the alcohol filtrates from the crystallizations.

Anal. Calcd. for $C_9H_9NO_4S$: neut. equiv., 113.6. Found: neut. equiv., 114.7.

The product was quinolinium hydrogen sulfate. Its water solution caused precipitation of barium ion. Krakau[6] listed its m.p. as 163.5–164.5°. Some of it was made by direct reaction of quinoline and sulfuric acid. Its m.p. (162–163°) was not depressed by admixture with the above material.

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(3) Sugasawa and Tsuda, *J. Pharm. Soc. Japan*, **56**, 103 (1936).

(4) Grosheintz and Fischer, THIS JOURNAL, **63**, 2021 (1941).

(5) Giacalone and Russo, *Gazz. chim. ital.*, **65**, 1125 (1935).

(6) Krakau, *J. Russ. Phys.-Chem. Soc.*, **17**, 364 (1885).

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Spectrophotometric Study of Reactions of Sodium Silicates with Sulfuric Acid and Ammonium Sulfate

BY R. C. MERRILL AND ROBERT W. SPENCER

The absorption spectrum of the cationic dye, pinacyanol chloride, in sodium silicate solutions depends on the form in which the silica is present **and thus varies with the silica to alkali (Na_2O)**

ratio.[1,2] These spectral differences have been used to follow the changes occurring prior to gelation on the addition of an ammonium salt or acid and to detect differences between silicates of the same analytical composition but different properties.

Figure 1 shows the absorption spectrum of 1.0×10^{-5} *M* pinacyanol chloride in a mixture of 0.01 *M* Na_2SiO_3 and 0.01 *M* H_2SO_4 after the acid–silicate mixtures had aged at twice this concentration for three minutes, one and five hours. The absorption spectrum changed gradually from that practically the same as in sodium metasilicate alone to the spectrum characteristic of the dye in a silicate with a silica to alkali ratio of 4 or 5 in mixtures aged for one hour.[2] The α and β bands at 600 and 548 mμ, respectively, almost disappeared and the γ band at 498 mμ became evident. During the subsequent fifteen hours the mixture changed so that the α and β bands of the dye's spectrum again became well defined and the γ band decreased in intensity and shifted to 514 mμ. Aging mixtures of 0.1 *M* $Na_2O \cdot 3.3SiO_2$ + 0.01 *M* H_2SO_4 produced a decrease in the intensity of the γ band of the dye in these solutions with an accompanying increase in intensity of the α and β bands. These changes were reversed after about twenty hours of aging. Such results indicate that a maximum effect on the absorption spectrum of the dye is observed with particles of an intermediate molecular weight.

The absorption spectrum of pinacyanol chloride was approximately the same in a 0.01 *M* $Na_2O \cdot 3.3SiO_2$–0.01 *M* $(NH_4)_2SO_4$ solution aged at twice this concentration for twenty-one hours as in a freshly prepared mixture. The absorption spectra were therefore determined in 0.025 *M* solutions aged at a concentration of 0.05 *M*. In contrast to the above results with sulfuric acid, the addition of 0.05 *M* ammonium sulfate to 0.05 *M* sodium metasilicate produced within three minutes a profound change in the nature of these solutions as shown by changes in the absorption spectrum of the dye in them after dilution. The α and β bands had almost disappeared and a prominent γ band appeared which increased somewhat in intensity on further aging. In mixtures of 0.05 *M* $(NH_4)_2SO_4$–0.05 *M* $Na_2O \cdot 3.3SiO_2$ only changes in the intensity of the γ band of the dye were observed until the solution gelled.

These differences in the behavior with pinacyanol chloride of acid–silicate and ammonium sulfate–silicate mixtures during aging suggest differences in the mechanism of gelation. This is in agreement with a suggestion made previously on the basis of differences in the effect of concentration and of acid or ammonium salt to silicate ratio on the time of set.[3] Gelation of a silicate–ammonium salt mixture may involve formation of a readily coagulated ammonium salt of a silicic acid of intermediate molecular weight as well as the condensation reaction occurring on the addition of an acid.

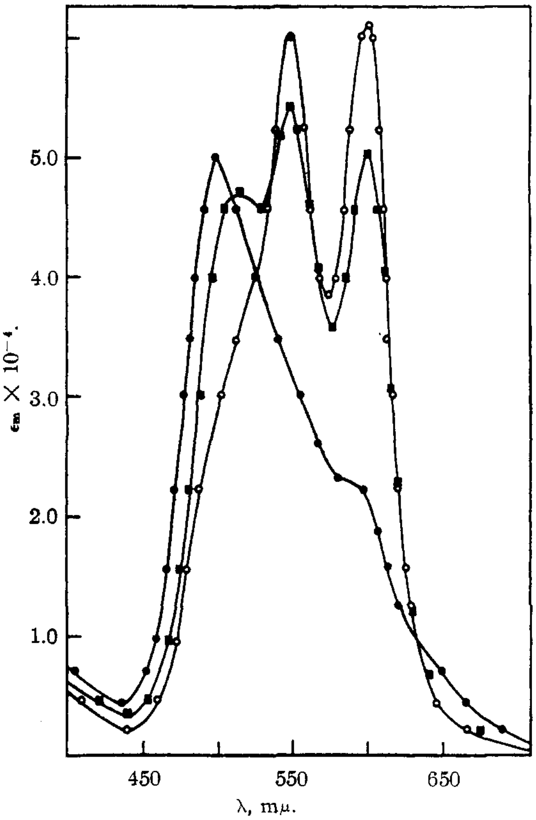

Fig. 1.—Molar extinction coefficients of 1.0×10^{-5} *M* pinacyanol chloride in 0.01 *M* Na_2SiO_3–0.01 *M* H_2SO_4 after acid–silicate mixture aged at twice this concentration for 3 min. – ○, 1 hr. – ●, and 5 hr. – ■.

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PHILADELPHIA, PA.
RECEIVED DECEMBER 16, 1949

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(1) R. C. Merrill, R. W. Spencer, and R. Getty, THIS JOURNAL, **70**, 2460 (1948).

(2) R. C. Merrill and R. W. Spencer, *ibid.*, **70**, 3683 (1948).

(3) R. C. Merrill and R. W. Spencer, *J. Phys. Colloid Chem.*, submitted.

The Preparation of 4-Ethyl-2-methoxy-2-phenylmorpholine

BY ROBERT H. JORDAN[1] AND ROBERT E. LUTZ

In our studies on ring-chain tautomerism of α-ethanolaminoketones[2] it was found that acid-catalyzed methanolysis of α-(ethylethanolamino)-acetophenone (Ia) gave readily and in good yield the cyclic acetal (Ib),[2b,d] and there was observed no evidence of the formation of significant amounts of any other product. The formation in

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(1) Postdoctorate Fellow (1948-1949), supported by a grant-in-aid from the National Institute of Health, recommended by the National Cancer Institute.

(2) (a) Lutz, Freek and Murphey, THIS JOURNAL, **70**, 2015 (1948); (b) a paper presented at the Chicago meeting of the American Chemical Society, April 20, 1948; (c) Lutz and Murphey, THIS JOURNAL, **71**, 478 (1949); (d) Lutz and Jordan, *ibid.*, **71**, 996 (1949).