allowed to cool at room temperature. The mixture was then added slowly to 15 ml. of sulfuric acid preheated to 60°, at such a rate that the temperature did not rise above 90°. When addition was complete the temperature of the reaction mixture was held at 90° for 20 min. and then allowed to fall to 60° when the mixture was poured with vigorous stirring over ice. The solid which separated was collected on a filter and then recrystallized from 500 ml. of alcohol with charcoal treatment to give 5.4 g. (30% yield) of a white solid (III), m.p. 216–218°. After further recrystallization it melted at 218–219°.

Anal. Calcd. for $C_{16}H_{19}NO_2$: C, 74.79; H, 7.44. Found: C, 74.83; H, 7.25.

α-Cyclopentylacetoaceto-*m*-anisidide which had been isolated was also converted in about 50% yield by treatment with sulfuric acid to III.

3-Cyclopentyl-7-methoxylepidine hydrochloride monohydrate (V). A mixture of 5.43 g. (0.021 mol.) of III and 5 ml. of phosphorus oxychloride was heated on a steam bath for about 30 min. until complete solution had almost taken place. The reaction mixture was heated at gentle reflux for 15 min. with a Bunsen burner and then it was poured into water with stirring. A solid separated which was collected on a filter and subsequently dissolved in chloroform. The solution was washed with water, and then dried over a sodium sulfate–sodium carbonate mixture. The drying agent was removed by filtration and the chloroform was removed *in vacuo* to leave a residual gum. The residue was dissolved in 40 ml. of glacial acetic acid. After the addition of 2 g. of anhydrous sodium acetate and 1 g. of 5% palladium on charcoal, hydrogenation was carried out at 35 lb. pressure with heat supplied to the flask by an infrared lamp. When the theoretical amount of hydrogen had been absorbed, the catalyst was removed and the volume of the filtrate was reduced. The residue was made basic with alkali. Extraction with ether and drying over a sodium hydroxide–sodium sulfate mixture gave an ether solution which was treated with hydrogen chloride gas to produce a solid. Recrystallization from alcohol gave 4 g. (70% yield) of off-white crystalline V, m.p. 210–211°.

Anal. Calcd. for $C_{16}H_{19}NO{\cdot}HCl{\cdot}H_2O$: C, 64.96; H, 7.50. Found: C, 65.05; H, 7.50.

Ethyl α-(3-oxocyclopentyl)acetoacetate (VI). A solution of 1.15 g. (0.05 atom) of sodium metal in 100 ml. of absolute alcohol was reduced in volume to dryness and the residue taken up in 4 ml. of absolute alcohol. Then a mixture of 22 g. (0.27 mol.) of 2-cyclopentenone[13] and 59.5 g. (0.46 mol.) of ethyl acetoacetate was added to the alcoholic solution with shaking. An exothermic reaction occurred. After 30 min. at room temperature, the reaction mixture was warmed at 45° for 2 hr. and then left at room temperature overnight. The reaction mixture was made neutral with 3.5 ml. of glacial acetic acid, diluted with 200 ml. of ether, and extracted twice with water. The ether extract was dried over sodium sulfate. Removal of the drying agent and distillation gave 38 g. (67% yield) of clear liquid (VI), b.p. 135° (1.5 mm.); n_D^{23} 1.4650. $\lambda_{max}^{CHCl_3}$ 1718 cm.$^{-1}$ (C=O); 1740 cm.$^{-1}$ (5-membered ring C=O); 1742 cm.$^{-1}$ (ester C=O); 1625 cm.$^{-1}$ (ester C=O chelated to enolic OH?).

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.32; H, 7.79.

3-(3-Oxocyclopentyl)-7-methoxy-4-methylcarbostyril (VII). A mixture of 5 g. (0.023 mol.) of ester VI and 2.9 g. (0.024 mol.) of *m*-anisidine was heated at reflux temperature over an open flame for 2.75 min. The thick red oil was poured into a beaker and allowed to cool. The oil was then chilled in ice and treated slowly with 23 ml. of concentrated sulfuric acid with stirring. The acid solution was left in ice for about 30 min., warmed on the steam bath for 10 to 15 min. and then poured with vigorous stirring over ice whereupon a gum separated. The suspension was made basic with sodium hydroxide solution so that the mixture became warm and the gum turned slightly crystalline. The mixture was neutralized with 10% hydrochloric acid and chilled in the ice bath for 3 hr. The solid was collected on a filter. Recrystallization from a 20:1 ethyl acetate–alcohol mixture gave a white solid (VII), m.p. 177–178°, 1 g. (15% yield).

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found: C, 70.56; H, 6.32.

The *2,4-dinitrophenylhydrazone* of VII was prepared and recrystallized from acetic acid,[16] m.p. 275–277° (dec.).

Anal. Calcd. for $C_{22}H_{21}N_5O_6$: C, 58.53; H, 4.69. Found: C, 58.13; H, 4.66.

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The Color of 8-Mercaptoquinoline

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The absorption spectrum of 8-mercaptoquinoline in ethanol and in 50% ethanol has been reported by Badger and Buttery[1] and observations concerning its thermochromic solution in chloroform containing a little ethanol were made. These workers considered that the C=C—C=S chromophore was not involved.

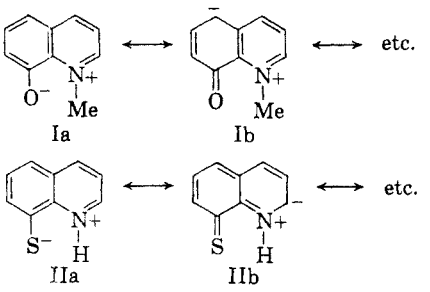
Very recently the absorption spectrum of 8-hydroxy-1-methylquinolinium anhydro salt (and of related compounds) in a number of solvents has been reported[2] together with some observations of the colors. Thus the hydrated 8-hydroxy-1-methylquinolinium hydroxide was orange, and this on dehydration changed to violet-red. The solution of the anhydro salt in water was red, in nonpolar solvents was violet, and the addition of hydroxylic solvents to the chloroform solution resulted in a progressive hypsochromic shift. End absorption in the visible was recorded for the acidic solution. A lucid explanation of these facts in terms of the resonance contributors (Ia), (Ib), *etc.*, the modification of these by hydrogen bonding at the oxygen atom, and of protonation of the oxygen atom has been presented.[2]

The generally similar shape of the spectra and the relative positions of the long wave length maxima of the 8-hydroxy-1-methylquinolinium anhydro salt (484 mμ)[2] and of the 8-mercaptoquinoline (500 mμ)[1] in ethanol together with some findings made during another investigation prompt us to record these observations in support of a parallel explanation of the properties of 8-mercaptoquinoline in terms of the resonance contributors (IIa), (IIb), *etc.* Thus the concentrated solution of 8-mercaptoquinoline in pyridine was an intense blue-violet which was changed by the addi-

(1) G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, 3236 (1956).

(2) J. P. Saxena, W. H. Stafford, and Winifred L. Stafford, *J. Chem. Soc.*, 1579 (1959).

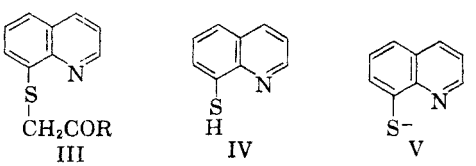
tion of ethanol to a reddish blue color; on the other hand, dilution of the concentrated solution with pyridine caused the color to be very greatly diminished.



The preparation of two *S*-alkyl type derivatives of 8-mercaptoquinoline is now reported. The reaction of phenacyl chloride with 8-mercaptoquinoline in pyridine solution gave 8-quinolyl phenacyl sulfide (III, R = C_6H_5); 8-quinolyl acetonyl sulfide (III, R = CH_3) was similarly prepared from chloroacetone and the thiol. Both of these compounds were colorless, either in the solid state or as their solution in organic solvents.

S-benzoyl 8-quinolyl sulfide, as reported previously,[3] was colorless. This compound gave a colorless solution in ethanol unchanged by the addition of water; however, this aqueous ethanolic solution gradually developed a red color, the more rapidly on warming. Thus it seems likely that the long wave-length absorption reported[1] for the benzoyl derivative in 50% ethanol should be attributed to the partial hydrolysis of this thiol ester, in which case the objection to the C=C—C=S chromophore for this substance is invalid.

Alkaline solutions of 8-mercaptoquinoline were colorless or nearly so, and the acidic solution was yellow confirming earlier observations.[3]



The above observations together with the change in the red color of the dihydrate to the pale violet color of the liquid 8-mercaptoquinoline[1] find a ready explanation in structure II. The existence in ionizing solvents of 8-mercaptoquinoline in the purple zwitterionic form is not unexpected in view of the greater acidity of thiol compounds as compared with hydroxyl compounds, this zwitterionic form being presumably modified in hydroxylic solvents and in the solid red dihydrate by hydrogen bonding. In nonpolar solvents the zwitterionic form would be relatively less stable (compare the *N*-heteroaromatic hydroxy compounds[4]) and the colorless nature of such solutions[1] finds explanation in the predominance of the tautomeric form (IV), the pale violet color of the pure liquid thus indicates an autoprotolytic equilibrium between IV and II. The effect of dilution of the pyridine solution can be attributed to a solvolytic equilibrium involving pyridinium ions and the anion (V), the latter entity accounting also for the lack of color of the aqueous alkaline solution of the thiol.

(3) A. Edinger, *Ber.*, **41**, 937 (1908).
(4) S. F. Mason, *J. Chem. Soc.*, 5016 (1957).

EXPERIMENTAL

S-Benzoyl 8-mercaptoquinoline was prepared by Edinger's method[3] and had m.p. 110° (lit.[3] 110°); preparation of this compound under nitrogen was found advantageous.

8-Quinolyl acetonyl sulfide. Chloroacetone was added to a solution of 8-mercaptoquinoline in pyridine and the solution was set aside overnight under nitrogen. The next day the mixture was stirred into water and the mixture was set aside for several days to crystallize. The solid was collected and purified by low temperature recrystallization from ethanol. The product was 8-quinolyl acetonyl sulfide, m.p. 54–54.5°.

Anal. Calcd. for $C_{12}H_{11}NOS$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.28; H, 4.97; N, 6.11.

8-Quinolyl phenacyl sulfide. Phenacyl chloride in pyridine was added to an equimolecular amount of 8-mercaptoquinoline in pyridine and the mixture was kept for 24 hr. under nitrogen and then poured into water to yield a solid. This solid was recrystallized from ethanol to give 8-quinolyl phenacyl sulfide m.p. 133°.

Anal. Calcd. for $C_{17}H_{13}NOS$: C, 73.12; H, 4.69; N, 5.02. Found: C, 73.01; H, 4.70; N, 4.76.

Acknowledgment. The author is indebted to Dr. W. Zimmermann and his staff for the microanalyses.

NOTE ADDED IN PROOF: Substantially similar conclusions concerning the color of 8-mercaptoquinoline have been reached by A. Albert and G. B. Barlin [*J. Chem. Soc.*, 2384 (1959)] in a paper which appeared after the submission of this note.

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Hydrogenolytic Cleavage of Menthofuran[1]

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Recently, Wienhaus[2] carried out the catalytic hydrogenation of menthofuran (I) over platinum black in acetic acid, reporting tetrahydromenthofuran (II) as the sole product. It is known, however, that in the presence of Adams' catalyst furan compounds are not only hydrogenated to tetrahydrofurans, but often subjected to hydrogen-

(1) Abstracted partly from the Master thesis submitted by W. Tagaki, March 1, 1956, and presented at the monthly meeting of Kansai Branch of the Agricultural Chemical Society of Japan, Kyoto, January 26, 1957.
(2) H. Wienhaus and H. Dewein, *Ber.*, **91**, 256 (1958).