and differs from that of the 2,5-hexanedione derivative. (Infrared spectra will not distinguish unequivocally between these two alternatives.)

Fractionation of a similar condensate on silica, without pretreatment, by the method of Bulen, Varner, and Burrell[6] yields a chromatogram with two major peaks (acetic and formic acids) and three minor peaks (two unidentified, one occurring at the position expected for levulinic acid). After passage of the crude reaction product over a silver oxide column[7] before fractionation, a new major peak appears at the position expected for levulinic acid. Its identification has been confirmed by comparison of the X-ray diffraction patterns of the silver salt and of the dinitrophenylhydrazone with those from authentic material.

Efforts to find 2,5-hexanedione in the neutral fraction after silver oxide treatment have not been successful. Control experiments showed that hexanedione was not oxidized to an acid by silver oxide at room temperature following the procedures used for oxidation of levulinaldehyde, or acid fractionation.

Gas-liquid chromatography on cyanoethylated glycerol, Apiezon L, or dioctyl sebacate–sebacic acid yields a large peak corresponding to levulinaldehyde. It gives evidence of only traces of material boiling higher. Hexanedione is readily separated from the aldehyde; if present at all as an oxidation product, it is formed in less than 5% of the yield of levulinaldehyde.[8]

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(6) W. A. Bulen, J. E. Varner, and R. C. Burrell, *Anal. Chem.*, **24**, 187 (1952).

(7) H. C. Bailey and J. H. Knox, *J. Chem. Soc. (London)*, 2741 (1951).

(8) We are indebted to H. N. Campbell for X-ray diffraction comparisons and to R. R. Hampton and R. G. Kiley for gas chromatographic analyses. This is communication No. 190 from the Research Center of the United States Rubber Company.

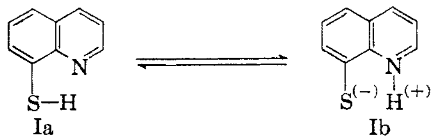
Solvolysis of *S*-Benzoyl-8-mercaptoquinoline and the Spectrum of 8-Mercaptoquinoline

Sir:

The preparation 8-mercaptoquinoline *via* Edinger's method[1] involves the isolation of its *S*-benzoate. Although the ester when recrystallized from ethanol appears to be a reddish crystalline solid, the use of chloroform for recrystallization results in the formation of colorless crystals. The pure, colorless ester will slowly solvolyze in hydroxylic solvents as Banfield surmised.[2] We have found the solvolysis to follow pseudo first order kinetics in anhydrous methanol and ethanol. The specific reaction rate constant of the ester methanolysis at 20° is approximately 1.4×10^{-5} sec^{-1} whereas the rate of the corresponding ethanolysis is at least one order of magnitude slower. We are now engaged in a detailed study of the kinetics of the *S*-benzoate solvolysis in various hydroxylic solvents and in the presence of various metal cations to probe the effect of chelate formation on the reaction rate.

In connection with the reactions of 8-mercaptoquinoline and its derivatives it is interesting to note the dramatic solvent effect upon the long wave-length absorption of 8-mercaptoquinoline itself. Pure anhydrous 8-mercaptoquinoline is a mobile hygroscopic blue liquid which takes on a purplish hue as it becomes wet. The completely hydrated compound ($+2H_2O$) is a red crystalline solid. The color of the anhydrous material varies from red violet in *t*-butyl alcohol to orange in aqueous solutions. In acidic or basic aqueous media the solutions appear yellow. Measurements of the visible absorption spectra yield the following results:

Solvent	λ_{max}, mμ	ϵ (l./mole cm.)
H_2O	448	2032
CH_3OH	490	133
C_2H_5OH	503	43
n-C_4H_9OH	509	27
$(CH_3)_3COH$	528	17



Ia Ib

The dramatic increase of the molar extinction with dielectric constant and the disappearance of the band in both acidic and basic aqueous solutions indicate that the species responsible is the dipolar ion (Ib). The dipolar ion would be formed in increasing concentration as a result of the shift of the equilibrium to the right with dielectric constant. The blue shift of the absorption band would seem to indicate an n-π transition of the dipolar form. If so, the unusually large molar extinction

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(1) A. Edinger, *Ber*, **41**, 937 (1908).

(2) J. E. Banfield, *J. Org. Chem.*, **25**, 300 (1960).

might reflect the greater degree of orbital overlap of the larger sulfur atom. An investigation on n-π transitions in other sulfur-containing compounds would be most interesting.

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