

ring have been studied in previous oxidation experiments<sup>3</sup>. The products of the oxidation reaction are at present being examined with the view of clarifying this point.

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<sup>1</sup> Ingles and Israel, *J. Chem. Soc.*, 810 (1948).

<sup>2</sup> Annual Reports, 78 (1922). Micheel and Micheel, *Ber.*, **65**, 253. Haworth, Lake and Peat, *J. Chem. Soc.*, 271 (1939).

<sup>3</sup> *loc. cit.* See also Myrbäck, *Svensk. Kem. Tidsk.*, **51**, 7, 74, 149, 179, 206, 225 (1939); **52**, 21, 200, 293 (1940).

### Stability of Aminobenzyl-Quaternary Salts

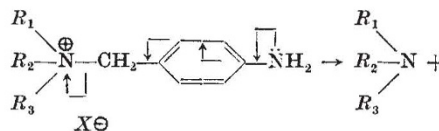
WHILE engaged in the preparation of benzyl-quaternary salts of a number of N-heterocyclic ring systems, the abnormal instability of some salts containing the aminobenzyl group was observed.

When, for example, *o*- or *p*-nitrobenzylquinolinium chloride was reduced under neutral conditions (ferrous hydroxide or iron powder and water), the desired amino-compound was difficult to isolate, and the only recognizable product (yield *c.* 80 per cent) was quinoline. The first conclusion, that here was a particularly facile case of reductive debenylation, had to be abandoned on further investigation. Thus, when *p*-nitrobenzylquinolinium chloride was hydrogenated in aqueous solution in the presence of palladium-charcoal and more than one mole of hydrochloric acid, six hydrogen atoms were absorbed, and the filtrate could be evaporated in a vacuum at a low temperature to leave *p*-aminobenzylquinolinium chloride hydrochloride as almost colourless hygroscopic crystals. In the dry state this was fairly stable over several weeks, and in solution it could be diazotized normally and coupled, for example, with  $\beta$ -naphthylamine in acid solution. The colourless solution of the hydrochloride, on treatment with sodium acetate, turned orange and deposited orange-yellow needles of the free amino-compound. This had a very low order of stability. It could be dried rapidly in a vacuum and analysed, but could not be recrystallized; warmed gently with water, it first dissolved but then rapidly decomposed to give quinoline in high yield and a brown amorphous material. In the dry state decomposition was apparent after a few days. Acetic anhydride converted the aqueous suspension into *p*-acetamidobenzylquinolinium chloride, a crystalline substance stable to boiling water.

On the other hand, *m*-aminobenzylquinolinium chloride hydrochloride, prepared in a similar manner to the *p*-isomer, was a non-hygroscopic substance, the aqueous solution of which was quite stable to boiling after the addition of sodium acetate. The free amino-quaternary iodide formed orange-red crystals from methanol.

Further work has since shown similar properties (*p*-amino, unstable; *p*-acetamido- and *m*-amino, stable) in the aminobenzyl-quaternary salts of isoquinoline, pyridine and phenyldimethylamine, as well as a number of *bz*-substituted quinolines. In the case of *p*-aminobenzylpyridinium chloride, the facile decomposition was probably observed by Lellmann and Pekrun<sup>1</sup>; but the significance was not explained.

It is suggested that the explanation for these observations may be that shown diagrammatically below; the strain in the benzyl-N bond due to the



presence of the adjacent positive charge is magnified to the point of actual rupture by the electromeric effect of a free amino-group in the *o*- or *p*-position. The greater stability of the *m*-isomer as well as that of the salts and acetyl-derivatives of the *o*- and *p*-isomers follows logically, while the amorphous substance which always accompanies the tertiary amine is seen to be probably the polymeric benzylene-imide.

It is hoped to publish fuller details of this work later.

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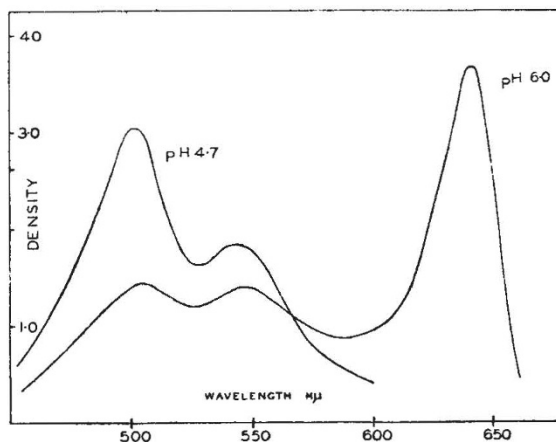
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Sept. 17.

<sup>1</sup> Lellmann and Pekrun, *Ann.*, **259**, 40 (1890).

### Use of Dyes to Determine the Iso-electric Point of Gelatin

THE effect of small concentrations of gelatin on the absorption characteristics of aqueous solutions of certain carbocyanine dyes has been reported by Sheppard<sup>1</sup> and Solovyev<sup>2</sup>.

During an investigation of some of the factors influencing the adsorption of these dyes to proteins, it was noted that the adsorption is electrostatic in character and depends upon the *pH* of the gelatin solution. Certain dyes exhibit a narrow and intense absorption band in the red region of the spectrum in dilute gelatin solutions (0.01 per cent) if the *pH* is above the iso-electric point. Below the iso-electric point the absorption is similar to that of the aqueous dye solution. The colour change is sharp and is illustrated by the absorption curves in the accompanying diagram.



The absorption of 1 : 50,000 3 : 3'-dimethyl 5 : 5'-dichloro-9-ethyl thiocarbocyanine chloride in 0.01 per cent aqueous gelatin solution at two *pH* values