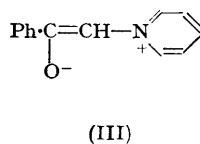
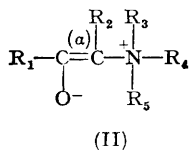
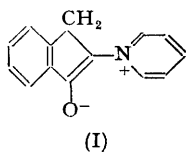


103. Two Enol Betaines of the Indane-pyridinium Series.

By W. H. STAFFORD.

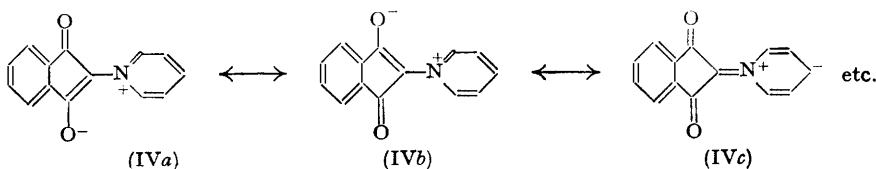
The syntheses and properties of the enol betaines (I) and (IV) derived from pyridine and indan-1-one and indane-1:3-dione respectively are described.

THE enol betaine (I) was obtained as an orange, crystalline hydrate by the action of dilute sodium hydroxide on an aqueous solution of 1-(3-hydroxyindan-2-yl)pyridinium bromide. The first evidence for the existence of compounds of the general enol betaine structure (II) was presented by Krollpfeiffer and Müller (*Ber.*, 1933, **66**, 739) who had isolated reactive, orange-coloured, highly crystalline compounds as intermediates in the "acid cleavage" of pyridinium salts derived from alkyl *o*- α -halogenoacylphenyl sulphides. This structure was subsequently confirmed by Kröhnke (*Ber.*, 1935, **68**, 1177) for the simpler product (III) from phenacylpyridinium bromide and in many subsequent papers for enol betaines in which $R_2 = H$, alkyl, or acyl. Although the reactions of these compounds have been exhaustively examined, their physical properties have been largely ignored.



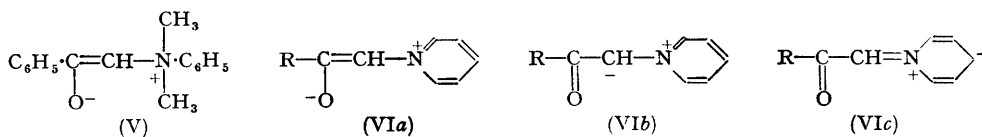
Crystallisation of the enol betaine (I) from aqueous methanol or ethanol under a variety of conditions gave a series of hydrates whose colour became less intense as the degree of hydration increased (cf. Kröhnke, *loc. cit.*; Kröhnke and Kübler, *Ber.*, 1937, **70**, 538). The problem of facile changes in hydration, combined with sensitivity to light, made reliable analyses difficult to obtain (cf. Krollpfeiffer and Müller, *Ber.*, 1935, **68**, 1169). The betaine

is soluble in ethanol, methanol, and to a lesser extent in water; it is only very slightly soluble in solvents such as benzene, chloroform, and ether. Solutions in ethanol are red when concentrated and yellow when dilute and do not fluoresce in ultra-violet light. The enol betaine is quite strongly basic and dissolves readily in dilute acetic acid and mineral acids, giving colourless solutions which fluoresce green in ultra-violet light. It may be recovered from acid solutions by making them slightly alkaline with caustic alkali. Specimens exposed to light darken quickly and solutions of these in acids are then slightly coloured; this may be due to photo-oxidation. Oxidation of the betaine with hydrogen peroxide yielded homophthalic acid (cf. Krollpfeiffer and Müller, *loc. cit.*).



The enol betaine (IV) from indane-1 : 3-dione was obtained directly by the action of alkali on the water-soluble product from the bromination of indane-1 : 3-dione in pyridine solution. Presumably bromination of the diketone (cf. Vona and Merker, *J. Org. Chem.*, 1949, **14**, 1048) was followed by the formation of the water-soluble pyridinium bromide by reaction with excess of pyridine (cf. King, McWhirter, and Rowland, *J. Amer. Chem. Soc.*, 1948, **70**, 239). This enol betaine was more soluble in non-polar solvents and was much more stable than was (I). It was recrystallised from methanol or aqueous ethanol and from the latter it showed no tendency to crystallise as a hydrate.

Although Kröhnke realised that the colour of the enol betaine could only be explained from the combination of the extended conjugated system and the polar nature of the molecule he made no deeper analysis of the problem. He did not, for example, attempt to explain the great difference in colour between the pyridinium enol betaine (III) and the anilinium enol betaine (V)—the latter is colourless. In the acylpyridinium enol betaines it seems reasonable to assume that, besides the two canonical forms (VIa) and (VIb), others, *e.g.*, (VIc), must contribute. The betaine (V) has two contributing structures



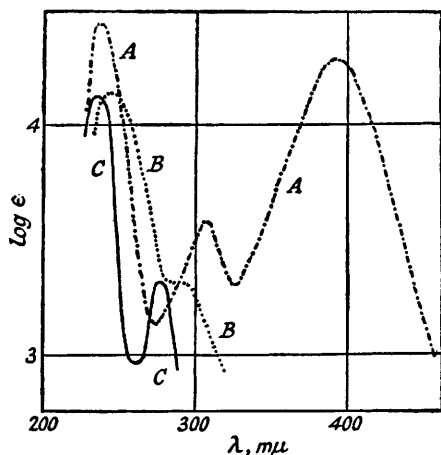
analogous to (VIa and b), but no contributing structures involving charge separation in the nitrogen-containing moiety are possible. This restriction in resonance is probably responsible for the differences in colour. The relative contributions of these various canonical forms are probably also responsible for the differences in colour and stability observed by Kröhnke in the phenacyl-pyridinium, -picolinium, -quinolinium, and -isoquinolinium series.

The absorption spectra of (I) in alcohol, water, and 0.1N-hydrochloric acid were determined. Extremely large discrepancies from the Lambert-Beer law were observed for alcoholic and, to a smaller extent, aqueous solutions. This was due to photochemical decomposition during the exposure to the arc—the solutions, initially yellow, rapidly faded. No reliance could therefore be placed on the values of $\log \epsilon_{\max}$, but the wave-lengths of the maxima were quite reproducible, *viz.*, 425 and 257 $m\mu$ in water, and 440 and 252 $m\mu$ in alcohol. The bathochromic shift for the absorption band in the visible region on change of solvent from water to ethanol is analogous to the change in the depth of colour of the hydrated crystals on alteration of the degree of hydration. The molecular environment in the crystal and in solution must affect the colour, probably by altering the effective contributions of the various dipolar canonical forms owing to differences in the dielectric

constant of the solvent or surroundings, the polarity of neighbouring molecules, or the susceptibility to induction or mutual induction of dipoles in neighbouring molecules.

In solution in dilute hydrochloric acid the enol betaine has an entirely different absorption spectrum (see figure). It is presumably the absorption spectrum of 1-(3-hydroxyinden-2-yl)pyridinium chloride, and comparison with the absorption spectrum of indan-1-one (Ramart-Lucas and Hoch, *Bull. Soc. chim.*, 1935, 2, 333) shows a reasonable similarity in form with a bathochromic shift.

The enol betaine (IV) is stable to ultra-violet light, and in ethanol solution has three prominent maxima and two minima (see figure). No change in absorption is observed in water or hydrochloric acid ($n/10$).



A, Enol betaine (IV) in ethanol or 0.1N-HCl.

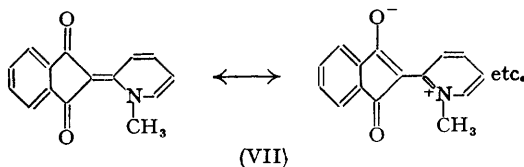
B, Enol betaine (I) in dil. HCl.

C, Indan-1-one in ethanol.

Unlike (I), it does not react with mercuric chloride, a fact clearly shown by the absorption spectrum of an ethanolic solution containing mercuric chloride (1%), which gave an absorption curve substantially the same as in ethanol alone except that the maximum at 238.5 $m\mu$ could not be observed owing to the complete absorption by the mercuric chloride below 270 $m\mu$.

The enol betaine (IV), like other α -acyl enol betaines is capable of the mesomerism indicated by (IVa and b). This possibility was clearly recognised by Kröhnke in the case of related compounds, and the diminished basicity is indicative of the existence of this resonance. In addition, other dipolar structures, e.g. (IVc), must contribute. An interesting comparison can be made between this enol betaine and "N-methylpyrophthalone" (VII) (Kuhn and Bär, *Annalen*, 1935, 516, 158), some of whose contributing structures are enol betaines.

In many recent papers on "meso-ionic" compounds (Baker *et al.*, *J.*, 1949, 307, etc.) certain compounds whose structure could only be represented as a hybrid of several ionic forms, dipolar in nature, have been discussed but Kröhnke and Kröllpfeiffer's enol betaines



have not been mentioned. The sydnone and related meso-ionic compounds are in fact enol betaines in so far as their principal contributing structures contain the general enol betaine structure (II) (cf. Hill and Sutton, *J.*, 1949, 452). The agreement between the proposed mechanisms of sydnone and enol betaine formation is also apparent, for both involve the removal of a hydrogen ion, in the former case by an acetate ion and in the latter by a hydroxyl ion (Baker *et al.*, *J.*, 1950, 1544).

EXPERIMENTAL

Absorption spectra were determined with a Hilger Barfit medium spectrograph.

1-(3-Hydroxyinden-2-yl)pyridinium Hydroxide Anhydro-salt,* the Enol Betaine (I).—2-Bromoindan-1-one (2.1 g.) in dry pyridine (5 ml.) was boiled for 1 minute. The brown opaque mixture resulting was taken up in water, and the excess of pyridine was removed by ether-extraction. The aqueous layer was made alkaline with cold sodium hydroxide solution (2N). Immediate separation of orange needles (1.7 g.) occurred. Recrystallisation from 90% methanol gave the enol betaine as irregular, red, rhombic prisms of the *hemihydrate* [Found: C, 76.4;

* For this nomenclature, cf. *J.*, 1950, 630.

H, 5.6; N, 5.8. $(C_{14}H_{11}ON)_2 \cdot H_2O$ requires C, 77.0; H, 5.5; N, 6.4%. Recrystallisation from 30% aqueous methanol gave slender orange needles of a *dihydrate* (Found: C, 68.9; H, 5.6. $C_{14}H_{11}ON \cdot 2H_2O$ requires C, 68.6; H, 6.2%). These hydrates lost water when heated above 100° and darkening occurred. Above 150° decomposition was apparent and the m. p. was dependent on the rate of heating, 170° being the highest value obtained (by rapid heating).

The enol betaine (0.1 g.) was oxidised by alkaline hydrogen peroxide (2 ml.; 0.5N-sodium hydroxide containing 10% of peroxide), to give a colourless solution; acidification after 24 hours gave homophthalic acid (0.035 g.), m. p. 180—181° (lit., 183°) alone or mixed with authentic material (Found: C, 59.5; H, 4.5. Calc. for $C_8H_8O_4$: C, 60.0; H, 4.5%).

The betaine formed an extremely insoluble, colourless mercurichloride which could not be purified as digestion with warm solvents caused decomposition to an insoluble coloured mass. The extreme insolubility was shown by mixing equal volumes of ethanolic solutions of the betaine (M/5000) and mercuric chloride (1%). An opacity followed by rapid coagulation leaving a colourless supernatant fluid occurred.

1-(1-Keto-3-hydroxyinden-2-yl)pyridinium Hydroxide Anhydro-salt, the Enol Betaine (IV).—A solution of bromine (0.75 ml.) in pyridine (5 ml.) was added to indane-1:3-dione (1.46 g.) in pyridine (2 ml.). After a few minutes' warming the solution was poured into water (100 ml.). The excess of pyridine was extracted with ether, and the coloured aqueous layer was made alkaline with 2N-sodium hydroxide. The dark solution slowly deposited the *enol betaine* as elongated yellow plates which crystallised from ethanol as elongated prisms (0.5 g.) with a yellow, metallic lustre, m. p. 255—256° (decomp.) (Found: C, 74.5; H, 3.9; N, 6.2. $C_{14}H_9O_2N$ requires C, 75.3; H, 4.1; N, 6.3%).

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