

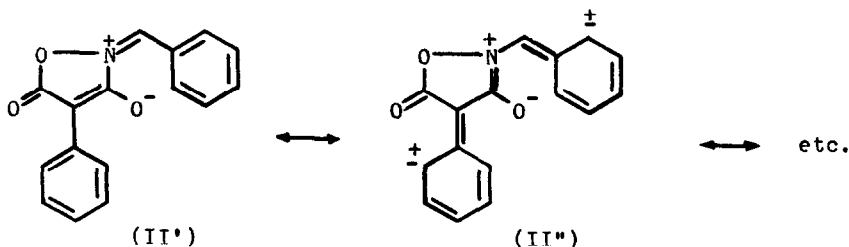
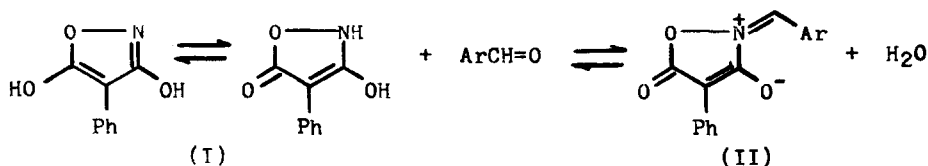
N-ARYLIDENEISOXAZOLONES. A NOVEL COLOURED  
IMONIUM ENOLATE STRUCTURE DERIVED FROM AROMATIC ALDEHYDES

Gury Zvilichovsky

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

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3,5-Dihydroxy-4-phenylisoxazole (I) which has been described recently<sup>1</sup> reacts with aromatic aldehydes to give red condensation products which are shown to be N-arylidene-4-phenylisoxazol-5-onium-3-enolates (II), in 50-100% yield.<sup>2</sup> The enolate charge is assumed to be located at the 3 position rather than at the 5 position because of the favourable conjugated structures (II', II'', etc.). The chromophoric properties of the isoxazolone ring have been previously illustrated in C-arylidene derivatives<sup>3,4</sup> and in 3-arylisoxazolone 4-azomethine derivatives.<sup>5-7</sup>



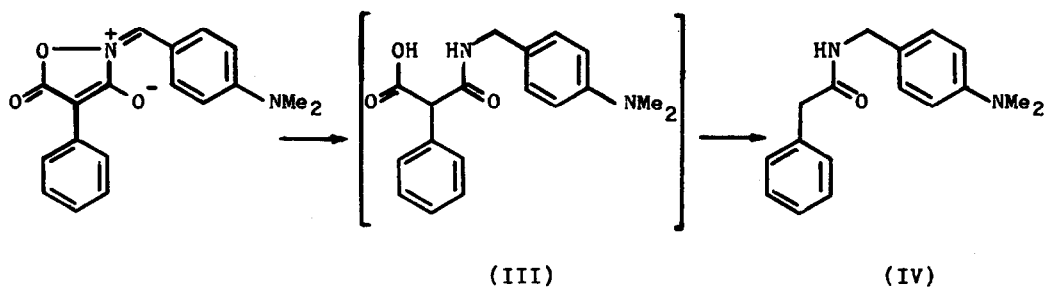
The reaction of I with benzaldehyde is spontaneous and takes place at room temperature in organic aprotic solvents like dioxane or tetrahydrofuran. The mechanism probably involves the protonation of the aldehydic oxygen by the very acidic enol of I.<sup>1</sup> The reaction is reversible and there is rapid decomposition in wet solvents back to I and benzaldehyde. The decomposition is easily followed by uv, vis and nmr spectroscopy. The crystallization of the red N-benzylidene-4-phenylisoxazol-5-onium-3-enolate (mp 215°<sup>2</sup>,  $\lambda$  max 480nm<sup>8</sup>) causes a shift in the equilibrium, resulting in quite high yields, even in the presence of small amounts of water. The nature of the reversibility was also proved by the isolation of I and of the 2,4-dinitrophenylhydrazone of benzaldehyde after the aqueous decomposition of the pure crystalline condensation product.

Benzaldehydes substituted with electron withdrawing groups, e.g. NO<sub>2</sub> or halogen, react slowly and pure products could not be isolated. Aldehydes with electron donating groups, e.g. OH, OMe or NMe<sub>2</sub>, react more readily and are more stable. Extended conjugation like in cinnamaldehyde also enhances stability and formation. The coloured crystals have a metallic luster, they do not dissolve in water, are slightly soluble in nonpolar organic solvents and more soluble in polar aprotic solvents. Their solutions are not stable and the colour fades with the age of the solution. Thus the molar extinction coefficients could not be accurately determined, they range from 2000 to 5000 except for the p-dimethylamino derivative (II, Ar=p-NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>) where  $\epsilon=25000$  and which is the most stable derivative of II.

The wavelength of the visible absorption changes with the type of substitution on the aldehydic component. Electron attracting groups cause a bathochromic shift (e.g. p-Cl,  $\lambda$  max 490nm), whereas electron donating groups shift the maxima to shorter wavelengths. The dimethoxy derivatives have maxima at 468 nm, salicylidene and vanillidene derivatives at 475 and 460nm respectively. There is an intense hypsochromic shift of the dimethylamino group ( $\lambda$  max 408nm<sup>8</sup>) in [p-dimethylaminobenzylidene]-4-phenylisoxazol-5-onium-3-enolate (mp 233°<sup>2</sup>) and a bathochromic shift in N-cinnamylidene-4-phenylisoxazol-5-onium-3-enolate which absorbs at a higher wavelength ( $\lambda$  max 525 nm<sup>8</sup>).

The infrared spectra of the red crystals in nujol show a strong band at  $1600\text{cm}^{-1}$  and two bands in the carbonyl region, one at  $1700\text{cm}^{-1}$  and a second in the range  $1760\text{-}1790\text{cm}^{-1}$ , depending on the aldehydic component. The dipole moment which was determined for N-cinnamylidene-4-phenylisoxazol-5-onium-3-enolate in dioxane (6.5D) is higher than that for the parent compound (I, 4.8D), indicating the dipolar features of these isoxazonium enolate derivatives.

The reduction with zinc in glacial acetic acid provided further support for the structure of II and a proof that the condensation is through the nitrogen. [p-Dimethylaminobenzylidene]-4-phenylisoxazol-5-onium-3-enolate which is stable in boiling acetic acid, was treated with zinc dust in boiling acetic acid to give 80% yield of IV (mp  $142^\circ$ ). Both the ring N-O and the  $\text{N}=\text{CH}$  bonds are reduced in these conditions and the reduction is followed by the decarboxylation of the intermediate malonamic acid (III). Elementary analysis and spectral properties are in agreement with structure IV. The unsubstituted



phenyl protons give a singlet while the substituted phenyl protons give 2 doublets; the  $\text{CH}_2\text{CO}$  methylene protons give a singlet at  $\delta$  3.80 and the  $\text{CH}_2\text{NH}$  methylenic protons show a doublet at  $\delta$  4.20 (in acetone- $d_6$ ). The latter doublet is changed into a singlet upon addition of  $\text{D}_2\text{O}$ , together with the elimination of the NH signal. Analogues of IV could be

obtained from 2,3- and 2,4-dimethoxybenzylidene derivatives (II, Ar=2,3- or 2,4-diOMe-C<sub>6</sub>H<sub>3</sub>- respectively) with zinc in boiling acetic acid but in poor yields.

Aromatic ketones do not yield red condensation products when they are brought together with I. Upon heating with I they give a slight yellow colouration. Saturated aliphatic aldehydes and ketones give a yellow colouration.  $\alpha,\beta$ -Unsaturated aldehydes give red colouration but solid coloured products could not be isolated.

#### References

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