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SYNTHESIS AND SPECTRA OF PYRYLO-TRIMETHINECYANINES

Alexandru T. Balaban
Department of Organic Chemistry, The Polytechnic, Bucharest, Roumania

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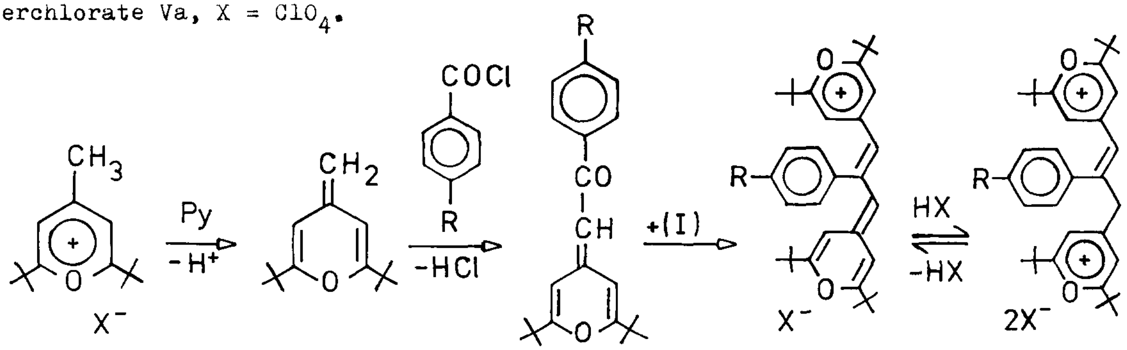
It was shown earlier that isobutene [1] and 2,3-dimethyl-2-butene [2] can be triacylated. In the case of isobutene, the product is a vinylogous 4-pyrone. On attempting to prepare similar vinylogous pyrones IV by acylating methyl-substituted pyrylium salts, dark blue compounds were obtained instead which proved to be pyrylo-trimethinecyanines V.

2,6-Di-t-butyl-4-methylpyrylium perchlorate (I) [3-5] was selected, since it has only one methyl group able to react. It was prepared [5] by leaving for 48 hrs a mixture of t-BuCl (1 mole), t-BuCOCl (2 moles) and $SnCl_4$ (1 mole) until HCl is no longer evolved, followed by 3 hrs' heating at 60°. Hydrolysis was effected by 500 ml hydrochloric acid (5 %) and benzene (200 ml). From the resulting three immiscible layers, the middle one was a pyrylium-benzene complex which, after steam distillation of benzene and treatment with $HClO_4$ afforded I, X = ClO_4.

Ten mmoles I, X = ClO_4, dissolved in 5 ml dry pyridine, were treated with five mmoles benzoyl chloride (IIIa) then refluxed for ten minutes. The deeply blue solution deposited on cooling pyridinium perchlorate, whose precipitation was completed by adding an equal volume of ether. The filtrate, on adding petroleum ether, deposited blue-black crystals with copper-like glitter, m. p. 259°, which were recrystallized from chloroform - petroleum ether, acetic acid, or benzene. By its elemental analysis and spectra, this product is the pyrylocyanine perchlorate Va, X = ClO_4.



(I) (II) (III) (IV) (V) (VI)

a, R = H ; b, R = Me ; c, R = OMe

IR spectrum (KBr pellet) : ClO_4^- (625, 1100 cm^{-1}) ; pyrylium ring vibration (1620 cm^{-1}) ; absence of strong bands in the 1630-2000 cm^{-1} range.

Visible absorption spectrum (in benzene) : 623 nm, lg ε 4.78.

^{1}H-NMR spectrum ($CDCl_3$, δ) : 1.17 (36H, s, t-Bu), 6.20 (4H, s, pyranic), 6.50 (2H, s, methine) and 7.2-7.8 (5H, m, Ph). The position and width of the pyranic proton peak depends on the solvent. This NMR spectrum indicates that the positive charge is delocalized making the two methinepyran moieties of V completely equivalent in all solvents which are not acidic.

However, the solution of Va in strong acids is colourless or pale yellow, evidencing the formation of the bis-pyrylium salt VIa, where the two moieties are no longer equivalent :

^{1}H-NMR spectrum (trifluoroacetic acid, δ) : 1.40 (18H, s, t-Bu), 1.51 (18H, s, t-Bu), 4.63 (2H, s, CH_2), 7.27 (1H, s, CH), 7.50 (2H, s, pyrylium), 7.77 (2H, s, pyrylium) and 7.3-7.8 (5H, m, Ph). Dilution with water or evaporation of the solvent causes the apparition of the blue colour.

With p-toluyl chloride (IIIb) or p-anisyl chloride (IIIc) instead of benzoyl chloride, analogous perchlorates were obtained, Vb and Vc, m. p. 264° and 262° respectively, absorbing at 622 and 620 nm in benzene (lg ε 4.6), respectively, both blue. Their ^{1}H-NMR spectra in $CDCl_3$, $D_3C-CO-CD_3$ or $D_3C-SO-CD_3$ have the methyl peaks at δ 2.47 (3H, s, Vb) and 3.90 (3H, s, Vc), the remaining peaks being similar to those of Va and the phenyl multiplet being replaced by A_2B_2 multiplets. Also, NMR spectra of VIb and VIc in TFA are similar to those of VIa.

We assume that methylenepyrans (anhydrobases) II and vinylogous pyrones IVa-c are intermediates in this simple synthesis of pyrylocyanines. This synthesis is similar to the reaction first observed by J. Kelemen and R. Wizinger-Aust using ethyl orthoformate instead of III, and 2,6-diisopropyl-4-methylpyrylium instead of I. Cyanines V dye polyacrylonitrilic fibres in bright blue colour.

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