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E.S.R. AND U.V. - SPECTROSCOPIC EVIDENCE OF A DONOR-ACCEPTOR COMPLEX PRESENT IN THE PYRIDINE SOLUTION OF TRIPHENYLPYRYLIUM PERCHLORATE.

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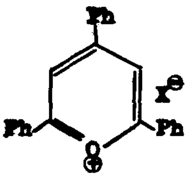
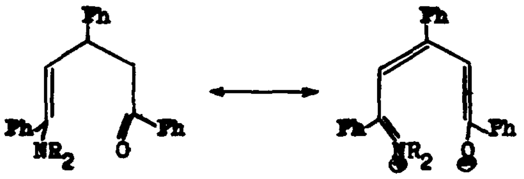
Triphenylpyrylium salts (I) react readily with primary and secondary amines, to give pyridinium salts and the acyclic adducts, II, respectively (1). Tertiary amines, in water or alcohols, convert I into the pseudobase III (1).



I



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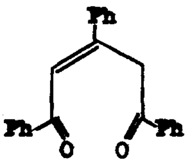
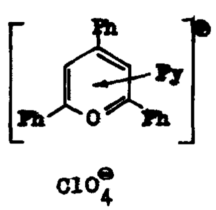


III

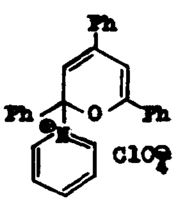
A: $X^\ominus = ClO_4^\ominus$

In order to investigate the behaviour of I towards anhydrous tertiary amines, where the formation of III is no longer possible, we studied the properties of the pyridine solution of triphenylpyrylium perchlorate (I A).

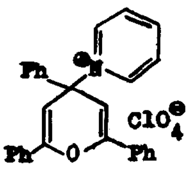
Excepting the trivial case when no reaction occurs, the products to be expected in this solution are the molecular (donor-acceptor) complex IV(2), the adducts V A,B and the valence isomer, VI. Compounds analogous to V A and VI are the reaction products of enamines with β-chlorovinylketones(3).



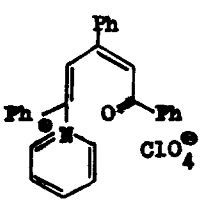
IV



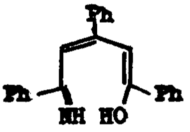
VA

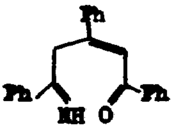


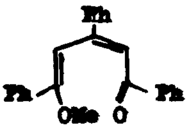
VB

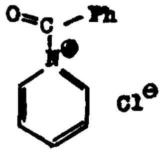


VI









By dissolving I A(1 g) in anhydrous pyridine (10-12 ml)one obtains a yellow solution. In a short time an E.S.R. signal (singlet,$g=2.0029 \pm$ $\pm$ 0.0001, half-line width $\Delta H_{1/2} = 4.29$ gauss) appears and increases slowly, reaching the maximum intensity after four days at room temperature.At the same time the solution changes its colour and finally becomes red. At 60°C both processes go to completeness in about three hours.

The solution thus obtained presents an absorption band at 310 mμ(X) No other band can be seen up to 650 mμ. The red colour is due to the tailing of the 310 mμ absorption band.

The complete disappearence of the triphenylpyrylium absorption bands (361 and 408 mμ in acetic acid (4), 360 and 405 mμ in dioxane or dimethylformamide) indicates that no more pyrylium salt exists in solution as such.

The position of the new peak coincides with that of the absorption band for the pseudobase III (298 mμ in 95 % ethanol (5), 310 mμ in pyridine)and is quite different from the position of the absorption band for the intermediate product (an equilibrium mixture of the iminoenol VII A (6a) and the unsaturated iminoketone VII B(6b))isolated by treatment of I A with ammonia. However, for the open chain structure VI the spectrum should be similar to that of the methyl ether VIII(λ_{max} 245 mμ with only an inflexion at 290 mμ, in ethanol (5))rather than with that of III.

(X) The U.V.spectra were studied at wavelengths over 300 mμ only because pyridine itself absorbs under 300 mμ.

Dilution with dioxane of the pyridine solution has little effect on the U.V.spectrum (in extremely dilute solution the absorption maximum is shifted to 305 m/u).

The infrared spectrum of the solution is difficult to interpret owing to the large excess of pyridine.It is noteworthy that all absorption bands (7) of the triphenylpyrylium perchlorate (IA) differing in position from those of the pyridine are present.However there are also present (with very low intensity) very weak absorption bands characteristic for compounds such as II,III,VII (1660, 1330, 1315, 1185,566 and 548 cm^{-1}).

The finding of triphenylpyrylium bands,together with the E.S.R. signal(X) and the deep modification of the U.V.spectrum indicate the donor-acceptor complex (IV) as the major component in the solution(the modification of the I.R.spectrum for donor-acceptor complexes are usually rather small (8))but it cannot completely preclude the presence of the other products V and VI. The " pseudobase - like absorption bands " in the I.R.spectrum can be due to small amounts of VI present in the mixture (or perhaps to some pseudobase III formed from I with traces of water still present).

Consequently, the 310 m/u absorption band in the U.V.spectrum is probably a charge-transfer band,characteristic of IV. It is possible that such donor-acceptor complexes,appear as transient intermediates in any reaction of pyrylium salts with nucleophiles but they undergo conversions into the subsequent intermediates or products (6a) too rapidly to be detected.

Finally, it is noteworthy that the transformations undergone by IA in pyridine solution are reversible. By pouring the pyridine solution into absolute ether, triphenylpyrylium perchlorate (IA) possessing the ultraviolet spectrum identical with that of the initial material(λ_{max} 275, 360 and

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(X) Another explanation for the paramagnetism of the solution would be the existence of such a complex with pyridine as donor,arising from the pyridinium compound VI. This fact seems improbable because the N-benzoylpyridinium compound IX (a lower double vinylogue of VI)obtained from benzoyl chloride in pyridine solution is not paramagnetic.

405 mμ in dioxane) is recovered almost quantitatively.

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