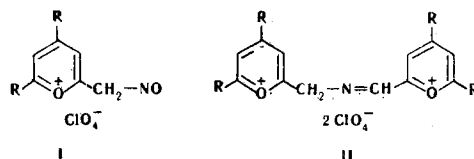


REACTION OF 2,4-DIARYL-6-METHYLPYRYLIUM SALTS
WITH NITRITE ESTERS

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We have found that with isoamyl nitrite 2,4-diaryl-6-methylpyrylium perchlorates form the nitroso compounds (I).



The reactivity of the nitroso groups in compounds (I) probably depends on the electron-donating properties of the substituents in the pyrylium nucleus. Thus, where $R = C_6H_5$, the main product of this reaction is the nitroso compound (I). But where $R = 4-CH_3OC_6H_4$ or $3,4-(CH_3O)_2C_6H_3$, the nitroso compound formed immediately condenses with the initial pyrylium salt to form the azomethines (II).

With an excess of isoamyl nitrite and brief heating in acetic anhydride, 2-methyl-4,6-diphenylpyrylium perchlorate forms 2-nitrosomethyl-4,6-diphenylpyrylium perchlorate (I), yield 93%, green prisms with mp 197-198°C (from acetonitrile). IR spectrum (paraffin oil), cm^{-1} : 1650, 1530, 1100, 940. UV spectrum (in CH_2Cl_2 , λ_{max} , nm (log ϵ): 270 (0.3), 380 (4.34), 400 (4.33).

We have been unable to observe the isomerization of (I) into an oxime (absorption band of the =N-OH group absent from the spectra).

With the initial pyrylium salt in acetic anhydride, (I) forms (4,6-diphenylpyrylio-2-ylmethyl)(4,6-diphenylpyrylio-2-yl-methylene)amine diperchlorate (II), yield 50%, dark-green prisms with mp 224-225°C (from glacial acetic acid). UV spectrum, λ_{max} , nm (log ϵ): 260 (4.36), 350 (4.65), 380 (4.80).

With isoamyl nitrite in acetic anhydride in the presence of sodium acetate, 2,4-di(p-methoxyphenyl)- and 2,4-bis(3,4-dimethoxyphenyl)-6-methylpyrylium perchlorates form the azomethines (II): [4,6-di(p-methoxyphenyl)pyrylio-2-ylmethyl][4,6-di(p-methoxyphenyl)pyrylio-2-ylmethylene]amine diperchlorate, yield 55%, dark-green prisms with mp 202-203°C (from glacial acetic acid); UV spectrum, λ_{max} , nm (log ϵ): 270 (4.60), 380 (4.87), 450 (5.24); and [4,6-bis(3,4-dimethoxyphenyl)pyrylio-2-ylmethyl][4,6-bis(3,4-dimethoxyphenyl)pyrylio-2-ylmethylene]amine diperchlorate, yield 75%, dark-green prisms with mp 241-242°C (from glacial acetic acid). UV spectrum, λ_{max} , nm (log ϵ): 270 (4.38), 300 (4.39), 350 (4.39), 420 (4.58), 480 (4.98). The results of elementary analysis for all the compounds obtained corresponded to the calculated figures.

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