REACTIONS OF 2- AND 4-(β-ETHOXYVINYL)PYRYLIUM SALTS WITH NUCLEOPHILES

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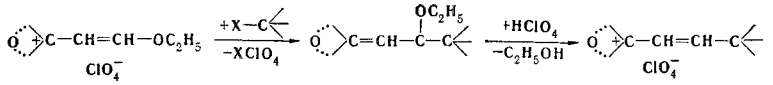
It has been shown that in reactions of 2- and 4-(β-ethoxyvinyl)pyrylium salts with nucleophiles such as active methylene compounds (acetylacetone, acetoacetic ester, dibenzoylmethane, malonic ester, phenylacetic acid, and cyanoacetic ester), charged heterocyclic systems containing α- or γ-methyl groups (pyrylium and pyridinium salts), vinyl ethers, enamines, active aromatic compounds (N,N-dimethylaniline, N,N-diethylaniline, anisole, phenetole, veratrole, and indole) and organomagnesium compounds, attack by the nucleophile is realized at the β-carbon atom of the β-ethoxyvinylpyrylium salt with subsequent splitting out of alcohol to form a conjugated system. Uncharged merocyanine dyes are formed with active methylene compounds, but in other cases a pyrylium salt with a new (in place of the ethoxy group) substituent is generated.



EXPERIMENTAL

Bisflavenetrimethylidyne Perchlorate. This compound (mp 286°) was obtained in 60% yield by condensation of 4-methylflavylium perchlorate with 4-(β-ethoxyvinyl)flavylium perchlorate.

2,4-Diphenyl-6-(δ-ethoxyvinyl)pyrylium Perchlorate. This compound (mp 170°) was obtained in 81% yield by heating 2,4-diphenyl-6-(β-ethoxyvinyl)pyrylium perchlorate (I) with ethyl vinyl ether in acetic acid.

2,4-Diphenyl-6-β-(2'-N-morpholino-1-cyclohexenyl)pyrylium Perchlorate. This compound (mp 178°) was obtained in 77% yield from I and 1-morpholino-1-cyclohexene in dichloroethane.

2,6-Diphenyl-4-styrylpyrylium Perchlorate. This compound [mp 252° (from acetic acid)] [1] was obtained in 69% yield from 2,6-diphenyl-4-(β-ethoxyvinyl)pyrylium perchlorate (II) and phenylmagnesium bromide.

2,6-Diphenyl-4-(p-dimethylaminostyryl)pyrylium Perchlorate. This compound (mp 288°) was obtained in quantitative yield by refluxing II and dimethylaniline in acetic anhydride.

Ethyl α-Cyano-γ-pyranylidenecrotonate. This compound (mp 152°) was obtained in 80% yield by refluxing I with cyanoacetic ester in acetic anhydride in the presence of sodium acetate.

The results of elementary analysis for C, H, N, and Cl were in agreement with the calculated values.

LITERATURE CITED

1. W. Dilthey and J. Fischer, Chem. Ber., 57, 1653 (1924).

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