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PREPARATION AND THERMAL BEHAVIOUR OF 1-SUBSTITUTED 2-DICYANOMETHYLENE-1,2-DIHYDROPYRIDINES: SYNTHESIS OF 2-PYRIDYL MALONONITRILES.

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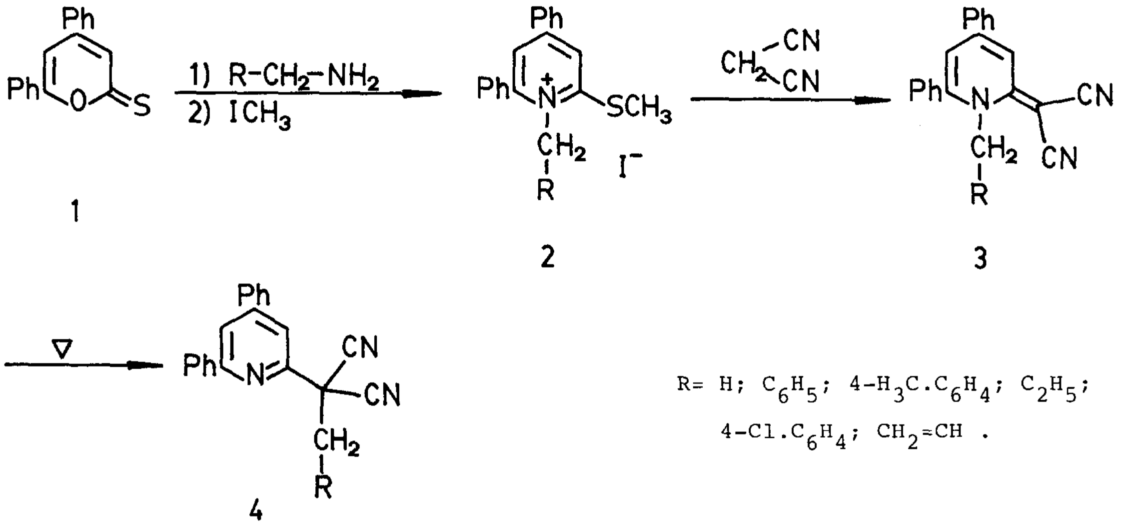
Summary: 1-Substituted 2-methylthio-4,6-diphenylpyridinium iodides (2) react with malononitrile under the influence of bases to give 1-substituted 1,2-dihydropyridines (3),which by thermal treatment can be converted into 2-pyridyl malononitriles (4).

4,6-Diphenylpyran-2-thione (1) is highly selective reagent for modification of primary amines in the presence of other functional groups: 1-substituted pyridinium salts formed undergo substitution at the CH_2 group α- to nitrogen with many nucleophiles[1].

We wish to report now the reaction of 1-substituted pyridinium salts (2) with malononitrile in the presence of base (triethylamine or pyrrolidine) to give the corresponding 1-substituted 2-dicyanomethylene-1,2-dihydropyridine (3) in very good yields (74-85%).The reaction can be perfomed in ethanolic solution at reflux temperature for 4-24 h. Support for the formulation (3) is clearly provided by their spectral data.The i.r. spectrum of compound (3, R=H; m.p. 205º ; 82%) shows two strong absorption bands at 2200 and 2190 cm^{-1} respectively,attributable to C≡N stretching; the ^{1}H-n.m.r. spectrum shows among others a singlet at δ 3.72 ppm corresponding to the N-CH_3 group; in the ^{13}C-n.m.r. spectrum the methyl group carbon appears at 44.3 ppm,the β-dihydropyridine ring carbons occurs at 135 and 134 ppm,the quaternary carbon linked to the cyano groups appears at 119.6 ppm,while the two cyano group carbons occurs at 116 and 115 ppm respectively.Mass spectrum shows the expected molecular ion peak and the fragmentation pattern is according with the proposed structure.

When compounds (3) are heated above their melting points under nitrogen for a short period of time,undergo rearrangement to give the corresponding 2-pyridyl malononitriles (4),which are isolated as orange crystals in excellent yields (68-81%).



R= H; C_6H_5; $4\text{-}H_3C.C_6H_4$; C_2H_5; $4\text{-}Cl.C_6H_4$; CH_2=CH .

The spectral data of malononitriles (4) support the structures assigned. Conpound (4, R=H; m.p.135°; 79%),shows a band at 2250 cm^{-1} in the i.r. spectrum due to the cyano group stretching; the proton n.m.r spectrum shows a sharp singlet at δ 2.35 ppm attributable to the methyl group,while the two β-pyridine protons appears as two doublets at δ 8.35 and 8 ppm respectively.The methyl group carbon shows up characteristically in the ^{13}C-n.m.r. spectrum at 25.52 ppm as do the cyano carbons group at 116.6 ppm,while the β-pyridine ring carbons occur near the benzenoid aromatic multiplet,the quaternary carbon linked to the cyano groups appears at 118.8 ppm.Mass spectrum is also in agreement with the structure (4).The conversion (3)⟶(4) seems to be general for arylmethyl,allyl and alkyl group; attempts with aryl groups failed to give (4).

REFERENCES:

1. P.Molina et al., Synthesis, 1982, 472; and references cited therein.

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