

SYNTHESIS OF HETEROCYCLIC COMPOUNDS
VII. 6-AMINO-2,4-DIARYL-3,5-DICYANO-4H-PYRANS¹

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Only few methods for 4H-pyran synthesis are known. In them, carbonyl compounds (2-4), pyrylium salts (5-7) or γ -pyrones (8,9) are used as starting materials.

In this paper a new synthesis of 4H-pyrans is described. α -Benzoylcinnamitriles, which are easily obtained from aromatic aldehydes and benzoylacetonitriles (10), react by Michael's addition with malononitrile. The resulting adducts cyclize through nucleophilic attack by the carbonyl oxygen at the cyano group. A series of new 4H-pyrans is thus obtained (Table I).

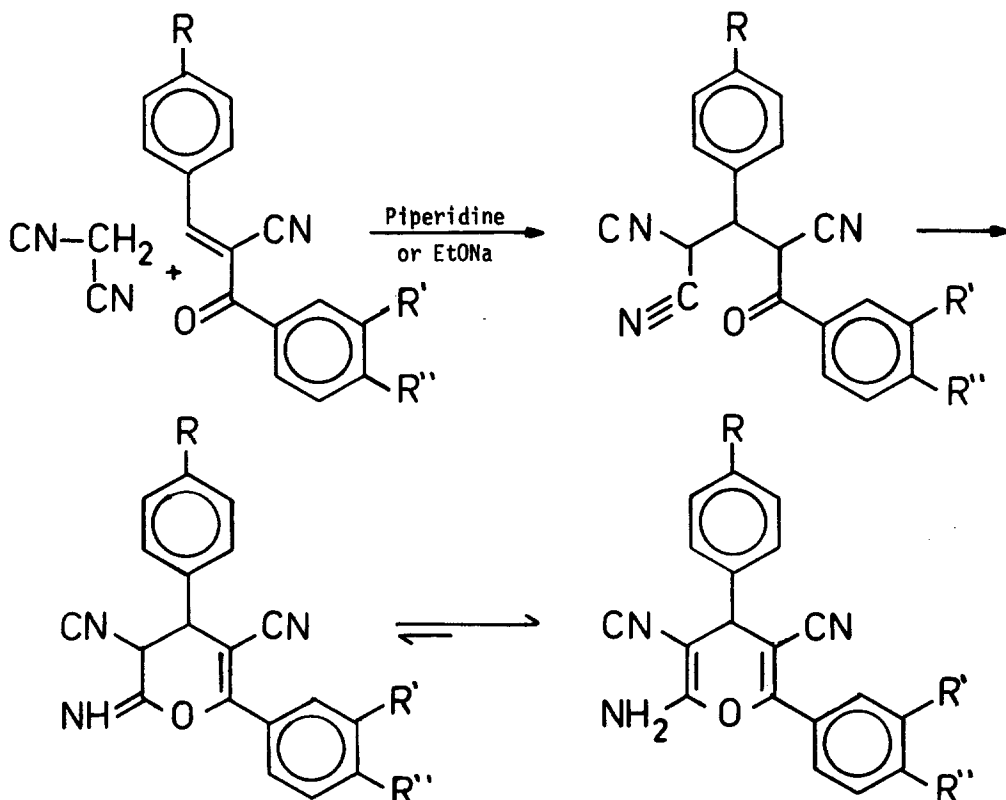


TABLE I. 6-AMINO-2,4-DIARYL-3,5-DICYANO-4H-PYRANS

R	R'	R''	m.p. (°C)	Yield (%)
H	H	H	181-182	91
Cl	H	H	175-176	84
OH	H	H	184-185	48
NO ₂	H	H	204-205	90
CH ₃	H	H	199-200	86
OCH ₃	H	H	199-200	73
H	NO ₂	H	211-212	83
H	H	Cl	209-210	71
H	H	CH ₃	195-196	82
NO ₂	H	OCH ₃	216-217	68
NO ₂	H	CH ₃	214-215	97
OCH ₃	H	CH ₃	216-217	87

The reaction is carried out in one step. Malononitrile, dissolved in an alcohol with a trace of a basic catalyst, is added to a suspension in alcohol of an equimolecular quantity of the α -benzoylcinnamitrile. After a few hours standing at room temperature, a high yield of 4H-pyran precipitates.

Structure elucidation is based on elemental analysis and spectra determinations. IR spectra, in all compounds, show a strong C=C band at 1660-1680 cm^{-1} and strong bands at 1135-1160 and 1250-1270 cm^{-1} , assigned to the ether linkage =C-O-C=, which are characteristic of the γ -pyran ring (2-6, 8-10). The NMR spectra show a singlet, $\delta = 4.15-4.9$, assigned to the proton at 4-position in the γ -pyran ring (4). Mass spectral data are also consistent with the structures assigned. UV spectra, in ethanol, show a single maximum at 296-300 nm.

Work in progress indicates that ethyl cyanoacetate reacts with α -benzoylcinnamitriles in the same way as malononitrile, yielding 6-amino-2,4-diaryl-5-carbethoxy-3-cyano-4H-pyrans.

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