

# Formation of Cyclohexylidene and Quinoline Products from 2-Methylpyran Derivatives

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6-Amino-4-aryl-5-cyano-2-methylpyran-3-carboxylates undergo cleavage and recombination when reacted with malononitrile, the products being 1-amino-3-aryl-2,6,6-tricyanocyclohexylidene-5-methylidenecarboxylates and related compounds.

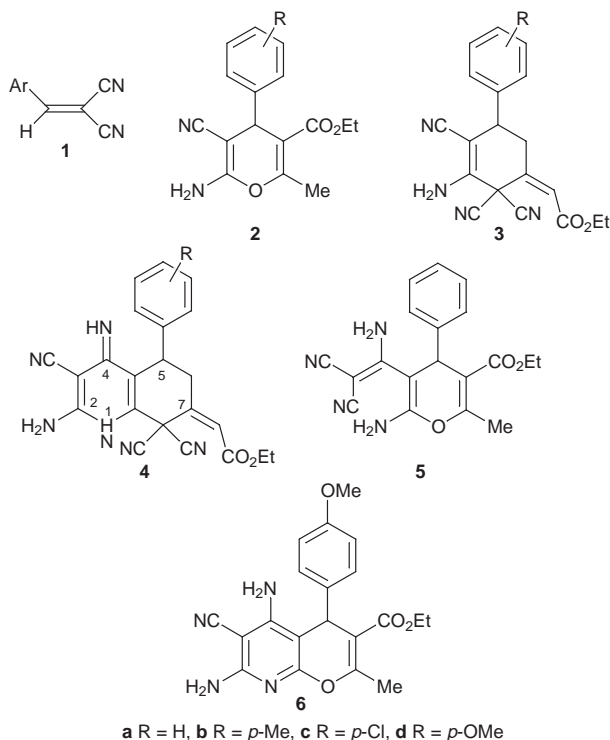
6-Amino-4-aryl-5-cyano-2-methylpyran-3-carboxylates **2** are readily obtainable from the reaction of conjugated dicyano compounds of type **1** with 3-ketobutanoates.<sup>1–3</sup> In recent years, several of these pyran compounds have been prepared and characterised, although one striking spectral feature—the complex appearance of the OCH<sub>2</sub> signal in the <sup>1</sup>H NMR spectrum—appears to have gone unrecorded. The presence of the chiral centre at C-4 has the effect of rendering the OCH<sub>2</sub> protons non-equivalent, so that they appear as an AB quartet ( $J = 11$  Hz) which is, of course, further coupled to the methyl protons ( $J = 7$  Hz).

Literature reports of the synthetic reactions of the pyran compounds **2** describe the preparation from them of pyranopyridine and pyranopyrimidine derivatives.<sup>2,4,5</sup> The only apparent case in which the pyran ring does not remain intact is the rearrangement which takes place in acid medium with formation of pyridin-2-one derivatives.<sup>3,6</sup>

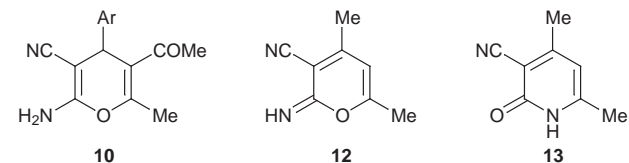
similar reaction occurs, but in these cases a second molecular equivalent of malononitrile also reacts, so that the products formed are the quinoline derivatives **4a** and **4b**.

Previous reports<sup>4,5</sup> that the reaction of pyrans **2** with malononitrile afforded pyrano **5** or pyranopyridine **6** structures have not been confirmed. The compounds formulated as **5** and **6** were not adequately characterised in the literature, but some of the physical and spectral data recorded resemble the data for **4a** and **3c** respectively. We believe that the formulations **5** and **6** were incorrect, and should be **4a** and **3c**.

It has also been claimed<sup>5</sup> that the reaction of the acetyl derivative **10** with malononitrile affords the iminopyran derivative **12**, but this product is properly formulated as the pyridin-2-one **13** (identical with the product which can be obtained from the reaction of 2,4-dioxopentane with cyanoacetamide<sup>8</sup>).



When, however, the pyran derivatives **2c** and **2d** react with malononitrile in the presence of piperidine, the products are the cyclohexylidene derivatives **3c** and **3d**. (Some of the starting material **2** is recovered unchanged, and intractable polymeric materials are also present.) When the phenyl and *p*-tolyl derivatives **2a** and **2b** are used, a



It is clear that the pyran structure **2** is considerably less stable than had been assumed.

Techniques used: IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, C–H COSY, NOE, HMBC

Schemes: 2

References: 11

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## References cited in this synopsis

- 1 N. M. Abed, E. A. A. Hafez, I. Elsakka and M. H. Elnagdi, *J. Heterocycl. Chem.*, 1984, **21**, 1261.
- 2 J. M. Quintela, C. Peinador and M. J. Moreira, *Tetrahedron*, 1995, **51**, 5901.
- 3 S. E. Zayed, E. I. A. Elmaged, S. A. Metwally and M. H. Elnagdi, *Collect. Czech. Chem. Commun.*, 1991, **56**, 2175.
- 4 N. M. Abed, N. S. Ibrahim and M. H. Elnagdi, *Z. Naturforsch., Teil B*, 1986, **41**, 925.
- 5 M. H. Elnagdi, R. M. Abdel-Motaleb, M. Mustafa, M. F. Zayed and E. M. Kamel, *J. Heterocycl. Chem.*, 1987, **24**, 1677.
- 6 M. M. Marugan, N. Martin, C. Seoane and J. L. Soto, *Annalen*, 1989, 145.
- 7 V. S. Hawaldar and S. V. Sunthakar, *Indian J. Chem., Sect. B*, 1980, **19**, 151.

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