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TETRAHEDRON
LETTERS

REGIOSELECTIVE SYNTHESIS OF [6c,12b-*cis*]-6c,7,12,13-TETRAHYDRO-1*H*-CHROMENO[3=B4, 4=B4 : 4,5]PYRANO[2,3-*c*]CHROMEN-1-ONES *VIA* UNUSUAL [1, 6] MICHAEL ADDITION.

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***Abstract*:**. 1-Aryloxymethylpyrano[2,3-*c*][1]benzopyran-5(3*H*)-ones (**1a-f**) on heating in N,N-diethylaniline suffered a [3s,3s] sigmatropic rearrangement followed by enolisation and an internal [1,6] Michael addition of the phenolic moiety to the diene-lactone moiety to give [6c,12b-*cis*]-6c,7,12b,13-tetrahydro-1*H*-chromeno[3=B4,4=B4 : 4,5]pyrano[2,3-*c*]chromen-1-ones (**2a-f**) in 65-75 % yield.

Recently there has been a flurry of activity on the synthesis of pyrano-pyrans[1]. In continuation of our work on the sigmatropic rearrangements of allylic and propynylic ethers of coumarin[2] we have recently reported[3] the regioselective synthesis of a series of 1-aryloxymethylpyrano[2,3-*c*][1]-benzopyran-5(3*H*)-ones (**1**). It occurred to us that a further investigation on the rearrangement of **1** which still possesses an allyl aryl ether moiety would provide polyheterocycles and would be interesting mechanistically.

Compound **1a**[3] was refluxed in N,N-diethylaniline for 8 h to give a crystalline solid, m.p. 224 ^{0}C, yield 75 % which has been characterised as 11-methoxy[6c,12b-*cis*]-6c,7,12b,13-tetrahydro-1*H*-chromeno[3=B4, 4=B4 : 4,5]pyrano[2,3-*c*]chromen-1-one (**2a**) from its elemental analysis and spectral data. The pyranopyran (6, 6) ring junction stereochemistry is found to be *cis* from NMR studies and also from molecular mechanics calculations. Encouraged by the results other substrates **1b-f** were also treated similarly to give pyranopyrans **2b-f** in 65-75 % yields.The formation of the products **2** from **1** may be easily explained by the [3,3] sigmatropic rearrangement of **1** to **3** followed by enolisation to give **4**. The phenol **4** in N,N-diethylaniline base may then add to the diene-lactone moiety by a [1, 6] Michael addition to give finally the product **2** (Scheme).

The present result seems to be quite unusual. Similar rearrangement studies have been reported on a number of analogous systems *viz.*, 4-aryloxymethyl-Δ^3-chromene is reported[4] to give the benzofuro[3,2-*c*]benzopyran, 7-chromenylmethyloxy-4-methylcoumarin gave mainly the angularly fused furopyran system,[5] and 7-chromenylmethyloxy flavone also gave exclusively the angularly fused furopyran system[6] whereas 4-aryloxymethylpyrano[3,2-*c*]coumarin gave only the phenolic product[7]. To our knowledge this is the first report on the formation of fused pyranopyran [6,6] ring from the [3,3] sigmatropic rearrangement and subsequent

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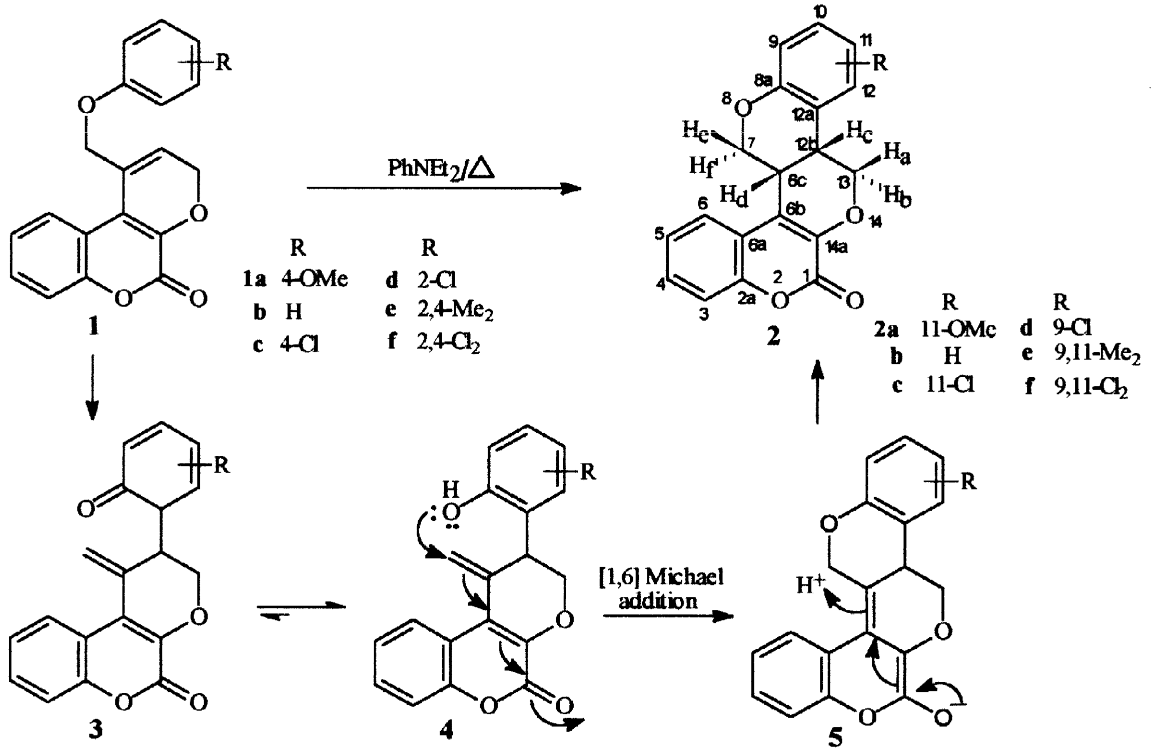

Scheme

cyclisation from an allyl aryl ether derivative.

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