A REGIOSPECIFIC SYNTHESIS OF 5-HYDROXY-2H,1-BENZOPYRAN

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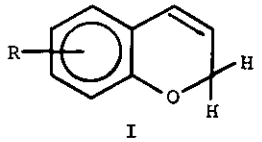
Abstract - The regiospecific synthesis of 5-hydroxy-2H,1-benzopyran, by the Claisen rearrangement of the arylpropargyl ether (6) is described.

2H-1-benzopyrans, (1), are very useful synthetic intermediates as they are easily converted into chromans, chroman-3-ones, chroman-4-ones, chromones[1] and coumarins[1].



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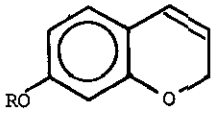
We have recently ascertained the optimum conditions for the preparation of these 2H, 1-benzopyrans by the the thermal rearrangement of arylpropargyl ethers, and in so doing made available 2H,1-benzopyrans substituted by electron withdrawing groups, which normally were unattainable via this simple Claisen rearrangement[2].

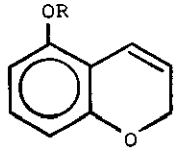
In the course of our work, we attempted the rearrangement of propargyl ethers of resorcinol and encountered a very useful example of regioselectivity which made 5-hydroxy-2H, 1-benzopyran, (2), available in good yield.

Whereas the arylpropargyl ether (3) was rearranged to a mixture of benzopyrans (4) and (5) in a 57% overall yield of benzopyran and in a ratio of 46:54 respectively[3], the arylpropargyl ether (6)[4] was rearranged in refluxing N,N-diethylaniline to only the benzopyran (7)[4] in 63% yield. The benzoate group can be removed by the standard hydrolytic methods.



4 : R = CH_3

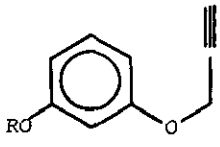
8 : R = Bz



2 : R = H

5 : R = CH_3

7 : R = Bz



3 : R = CH_3

6 : R = Bz

The structure (7) as opposed to (8), was favoured by an analysis of the NMR spectrum of the material, which showed H-2 at δ 4.75 (2H, dd, J = 3.0 and 1.7 Hz) H-3 at δ 5.70 (1H, pair of t, J = 10.0 and 3.0 Hz) and H-4 at δ 6.43 (1H, pair of t, J = 10.0 and 1.7 Hz) [c.f. the NMR spectrum of (4): H-3 at δ 5.52 (1H, pair of t, J = 9.5 Hz) and H-4 at δ 6.28 (1H, pair of t); and the NMR spectrum of (5): H-3 at δ 5.58 (1H, pair of t, J = 9.5 Hz), H-4 at δ 6.66 (1H, pair of t)[3]]. Thus the oxygen attached to C-5 (peri to H-4) deshielded H-4 through a diamagnetic anisotropic effect and this feature was used diagnostically.

We are not able to rationalise the regioselectivity encountered here, in terms of simple steric or electronic factors.

References

1. V.G.S. Box, B.A. Burke and C. McCaw, unpublished work.
2. V.G.S. Box and C. McCaw, Revista Latinoamer. de Quimica, in press.
3. W.K. Anderson and E.J. LaVoie, J. Org. Chem., 1973, 38, 3832.
4. This compound gave satisfactory spectral data (IR, UV and NMR) which could be unequivocally interpreted in terms of the given structure. No elemental analyses were thought necessary.

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