

# On the Preparation of 2-Benzopyrylium-4-oxide and its Cycloaddition Properties

Peter G. Sammes\* and Richard J. Whitby

Department of Organic Chemistry, The University, Leeds LS2 9JT, U.K.

Treatment of 1-acetoxy-1*H*-2-benzopyran-4-one with either base or heat generates the parent 2-benzopyrylium-4-oxide system which gives intermolecular cycloadducts with a variety of dipolarophiles, including olefins.

Heating or irradiating 2,3-diphenyl-2,3-epoxyindenone is well known to give the relatively stable ylide 1,3-diphenyl-2-benzopyrylium-4-oxide<sup>1</sup> and its cycloaddition reactions with a variety of dipolarophiles have been studied.<sup>2</sup> Previously, however, cycloadditions to the synthetically more useful parent benzopyrylium system have not been reported. Although Feldman has recently described a photochemical route<sup>3</sup> to intramolecular adducts that may be formed *via* substituted analogues of this zwitterion, competing photochemical reactions were also observed and an attempt to trap the parent system by photolysis of 2,3-epoxyindenone failed.<sup>4</sup> An alternative route to the title compound, involving oxidation of isochromanone derivatives, followed by reaction with acid gave only dimers and polymers.<sup>5</sup> The related 1-methoxy-2-benzopyrylium-4-oxide has been formed by copper catalysed decomposition of *o*-methoxycarbonyl- $\alpha$ -diazoacetophenone and some of its cycloaddition reactions observed.<sup>6</sup>

Herein we describe a simple route to the parent 2-benzopyrylium-4-oxide (6) from the benzannelated pyranoside (5), which follows our previous work on 3-oxidopyrylium.<sup>7</sup> This method avoids the need to prepare the relatively unstable indenone oxides and is applicable to intermolecular cycloadditions.

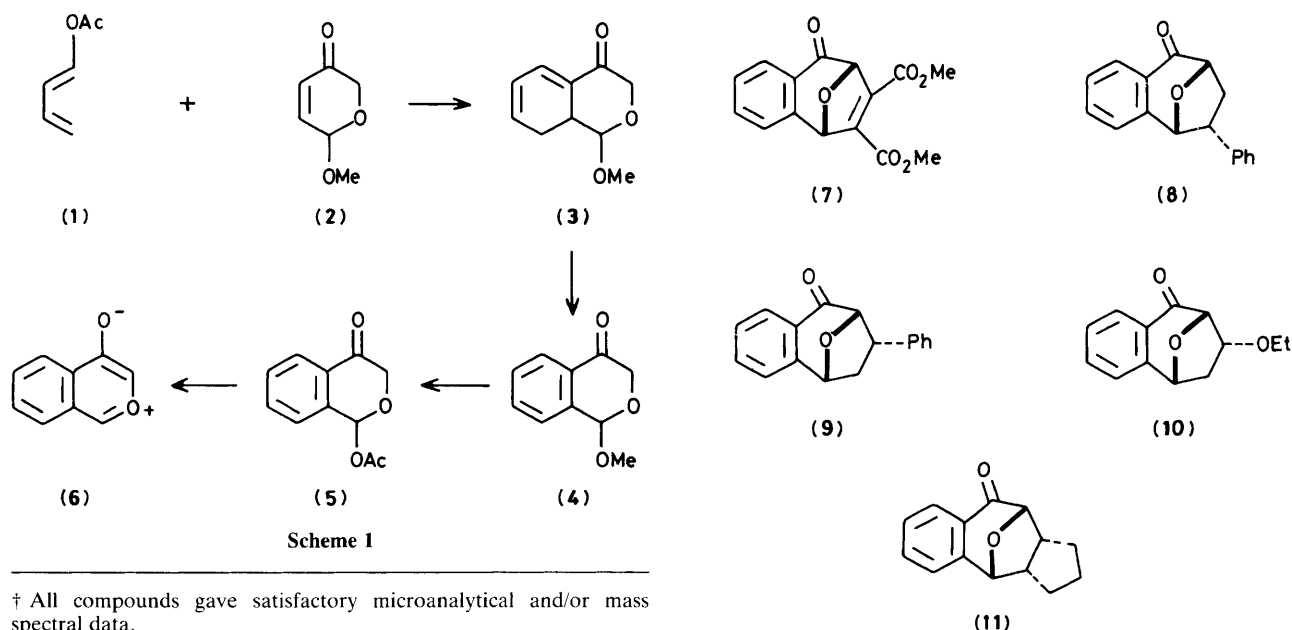
Cycloaddition of 1-acetoxybutadiene (1) to 6-methoxy-pyran-3(6*H*)-one (2), followed by treatment with triethylamine, afforded the cyclohexadiene (3) (80% yield).<sup>†</sup> Dehydrogenation with palladium on charcoal afforded the benzopyranone (4) (54% yield),<sup>8</sup> which could be hydrolysed with acid then acetylated to give the required acetate (5) (Scheme 1).

Treatment of the acetate (5) with either base or heat generated the reactive intermediate (6), which could be trapped with a wide range of dipolarophiles. For example,

dimethyl butynedioate gave the 1:1 adduct (7) in 88% yield. With styrene two main cycloadducts were isolated in 48% and 37% yield. <sup>1</sup>H N.m.r. studies<sup>7</sup> showed that these were the regioisomeric *endo*-adducts (8) and (9) respectively. The lack of regiocontrol in this instance, as compared to the single isomer observed in the reaction between 3-oxidopyrylium and styrene,<sup>7</sup> is in accord with simple Hückel molecular orbital calculations which indicate that the HOMO-LUMO and LUMO-HOMO interactions between dipole and dipolarophile are approximately equal and predict opposite regiochemistries. Small quantities of the *exo*-adducts were also isolated from the reaction mixture.

The reaction of (6) with ethyl vinyl ether gave the single *endo*-adduct (10) (60% yield), again the reverse regiochemistry to that observed in the 3-oxidopyrylium series.<sup>7</sup> Even cyclopentene reacts with the ylide (6) to give two products identified as the *endo*-adduct (11) (70%) and the *exo*-isomer (8%). The stereochemistry of these adducts followed from their proton n.m.r.s, in particular one of the cyclopentane ring protons in the *endo*-isomer (11) is shifted up to  $\delta$  0.5 by the aromatic ring current. The preference for the transition state leading to the *endo*-adduct is noteworthy since there are no secondary orbital interactions to consider. Presumably attractive benzo-ring-alkyl interactions are operating in favour of the *endo*-transition state.<sup>9</sup> Cyclohexene also reacts to give a low yield (10%) of the *endo*-adduct.

2-Benzopyrylium-4-oxide may thus be readily generated and forms 1:1 adducts with electron rich, electron poor, and electronically unbiased dipolarophiles. The fusion of a benzene ring to 3-oxidopyrylium as in (6) is seen to impart two effects, (i) to inhibit dimerisation, thus allowing less reactive dipolarophiles to react, and (ii) to change the ratio of the regioisomers formed.



<sup>†</sup> All compounds gave satisfactory microanalytical and/or mass spectral data.

We thank the University of Leeds for a research studentship (to R. J. W.).

Received, 2nd March 1984; Com. 282

### References

- 1 E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.*, 1964, **86**, 3814.
  - 2 J. W. Lown and K. Matsumoto, *Can. J. Chem.*, 1971, **49**, 3443.
  - 3 K. S. Feldman, *Tetrahedron Lett.*, 1983, **24**, 5585.
  - 4 K. Undheim and B. P. Nilsen, *Acta Chem. Scand., Ser. B*, 1975, **29**, 503.
  - 5 B. P. Nilsen and K. Undheim, *Acta Chem. Scand., Ser. B*, 1976, **30**, 619.
  - 6 T. Ibata and J. Troyoda, *Chem. Lett.*, 1983, 1453.
  - 7 P. G. Sammes and L. J. Street, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1261.
  - 8 P. J. Card, *J. Org. Chem.*, 1982, **47**, 2169.
  - 9 D. W. Jones and G. Kneen, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1647.
-