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

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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[1] and its cycloaddition reactions with a variety of dipolarophiles have been studied.[2] Previously, however, cycloadditions to the synthetically more useful parent benzopyrylium system have not been reported. Although Feldman has recently described a photochemical route[3] 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.[4] An alternative route to the title compound, involving oxidation of isochromanone derivatives, followed by reaction with acid gave only dimers and polymers.[5] The related 1-methoxy-2-benzopyrylium-4-oxide has been formed by copper catalysed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone and some of its cycloaddition reactions observed.[6]

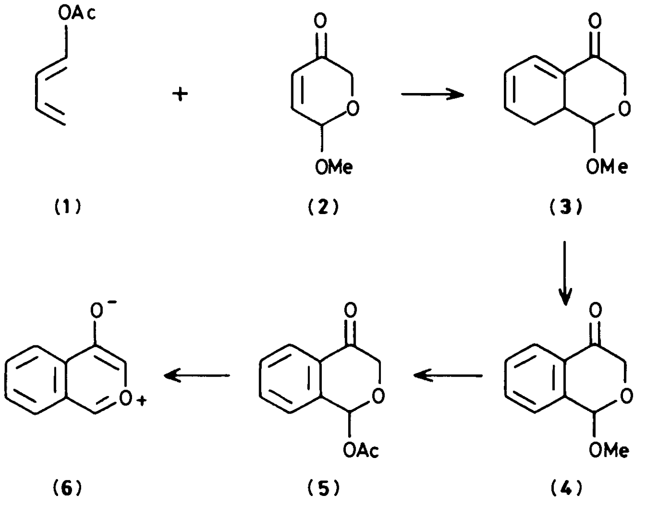
Herein we describe a simple route to the parent 2-benzopyrylium-4-oxide (**6**) from the benzannelated pyranoside (**5**), which follows our previous work on 3-oxidopyrylium.[7] This method avoids the need to prepare the relatively unstable indenone oxides and is applicable to intermolecular cycloadditions.

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

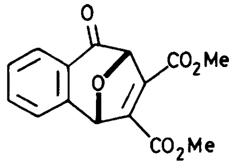
Treatment of the acetate (**5**) with either base or heat generated the reactive intermediate (**6**), which could be trapped with a wide range of dipolarophiles. For example, dimethyl butynedioate gave the 1 : 1 adduct (**7**) in 88% yield. With styrene two main cycloadducts were isolated in 48% and 37% yield. ^{1}H N.m.r. studies[7] 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,[7] 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.[7] 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 δ 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.[9] Cyclohexene also reacts to give a low yield (10%) of the *endo*-adduct.

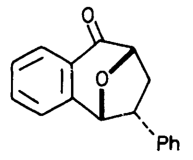
2-Benzopyrylium-4-oxide may thus be readily generated and forms 1 : 1 adducts with electron rich, electron poor, and electronically unbiased dipolarophiles. The fusion of a benzene ring to 3-oxidopyrylium as in (**6**) is seen to impart two effects, (i) to inhibit dimerisation, thus allowing less reactive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



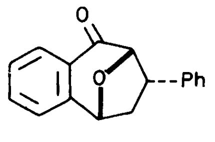
Scheme 1



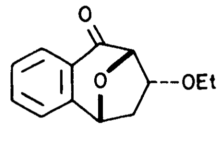
(**7**)



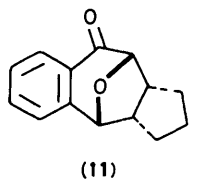
(**8**)



(**9**)



(**10**)



(**11**)

[†] All compounds gave satisfactory microanalytical and/or mass spectral data.

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