Studies of [3,3]Sigmatropic Rearrangements: Rearrangement of 3-(4-*p*-Tolyloxybut-2-ynyloxy)[1]benzopyran-2-one

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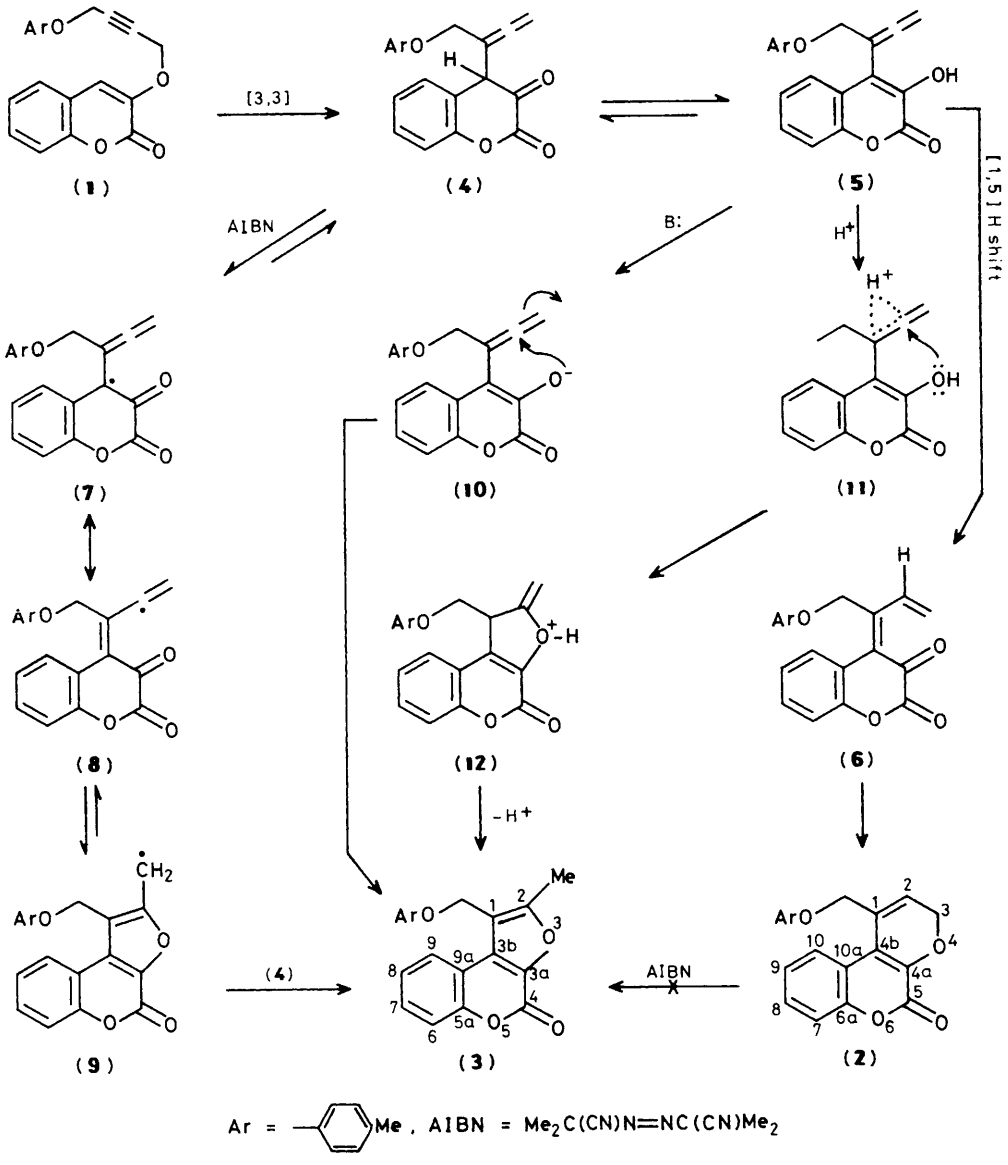
3-(4-*p*-Tolyloxybut-2-ynyloxy)[1]benzopyran-2-one (**1**), when refluxed in chlorobenzene, ethyl benzene, or xylene, gave exclusively 1-(*p*-tolyloxymethyl)pyrano[2,3-*c*][1]benzopyran-5(3*H*)-one (**2**), whereas through an ionic or radical pathway 2-methyl-1-(*p*-tolyloxymethyl)furo[2,3-*c*][1]benzopyran-4-one (**3**) was the exclusive product.

3-Alkyl and 4-alkyl coumarins ([1]benzopyran-2-ones) are reported[1—4] to have anthelmintic, hypnotic, insecticidal, antifungal activities and anticoagulant effect on blood. A considerable amount of work has been done on the synthesis of these compounds, but not much on the synthesis of 3,4-fused coumarins.[5—7] Recently we have achieved the regioselective synthesis[8] of 4-aryloxymethyl pyrano [3,2-*c*]-[1]benzopyran-2-ones from 4-(4-aryloxybut-2-ynyloxy)-[1]benzopyran-2-ones. Here we report the results of the [3,3]-sigmatropic rearrangement of 3-(4-*p*-tolyloxybut-2-ynyloxy)[1]benzopyran-2-one (**1**) (Scheme 1).

Compound (**1**), m.p. 155 °C, was synthesised from 4-chloro-1-(*p*-tolyloxy)-but-2-yne and 3-hydroxy[1]benzopyran-2-one in anhydrous Me_2CO–K_2CO_3 (yield 80%). The product (**1**) was refluxed in carefully purified‡ chlorobenzene (b.p. 132 °C) for 4 h, then chlorobenzene was removed *in vacuo* and the crude mass was subjected to column chromatography over

† The homodecoupling, ^{13}C n.m.r., and heteroatom correlation (HETCOR) experiments on compound (**3**) were performed by Dr. A. Patra.

‡ The solvents, chlorobenzene, ethylbenzene, and xylene were purified by successively washing with dil. H_2SO_4, dil. NaOH, water, and freshly prepared iron(II) sulphate solution, dried (Na_2SO_4), refluxed with hydroquinone, and distilled twice before use.



Scheme 1

silica gel. The exclusive product was 1-(*p*-tolyloxymethyl)pyrano[2,3-*c*][1]benzopyran-5(3*H*)-one (**2**) (yield 92%; m.p. 135 °C). The same reaction in refluxing ethylbenzene (b.p. 136 °C) or xylene‡ (140 °C) for 4 h also gave the product (**2**) exclusively; no furo[2,3-*c*]benzopyran-4-one was obtained.

We then studied the rearrangement of (**1**) in the presence of a radical initiator. When compound (**1**) was heated in chlorobenzene‡ in the presence of azobisisobutyronitrile (AIBN) (5 mg) for 2.5 h, 2-methyl-1-(*p*-tolyloxymethyl)-furo[2,3-*c*][1]benzopyran-4-one (**3**), m.p. 194 °C, was obtained in 80% yield, along with a 20% yield of (**2**). Compound (**3**) was characterised by elemental analysis and spectral data and the structure was confirmed by homodecoupling, ^{13}C n.m.r., and HETCOR experiments. Protonated carbon resonance assignments were established by direct correlation with proton resonances by HETCOR with normal one-bond C–H coupling, and non-protonated carbon resonances were established by a long-range (*J* 7 Hz) HETCOR experiment (primarily three-bond coupling). The benzene ring methyl proton resonance was correlated with the carbon resonances of C-3′ and C-5′. The 2-methyl proton resonance was correlated with the non-protonated carbon resonance of C-1. The 1-CH_2 proton resonance was correlated with the non-protonated carbon resonances of C-3b and C-2. The aromatic C-9 proton was correlated with the non-protonated carbon resonances of C-5a and C-3b.

When compound (**1**) was heated at 140 °C for 4 h in non-polar solvents, *viz.* polyethylene glycol (PEG-600) or *N*,*N*-dimethylaniline, the furo[2,3-*c*]benzopyran-4-one (**3**) was obtained in 90% yield. When (**1**) was refluxed in pyridine (116 °C) for 20 h an 80% yield of (**3**) was obtained along with 20% of unchanged starting material. When (**1**) was refluxed in ethylbenzene (140 °C) in the presence of toluene-*p*-sulphonic acid, (**3**) was again obtained, in 90% yield. In these cases no pyrano[2,3-*c*]benzopyran-5-one was obtained.

A possible mechanism[9,10] for the formation of (**2**) and (**3**) is outlined in Scheme 1.

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