The Oxidative Cyclisation of Allyl Aryl Ethers to 3-Chromanols

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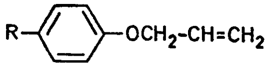
Summary Treatment of certain allyl aryl ethers with thallium(III) sulphate in 2·0—2·5M-sulphuric acid gave the corresponding 3-chromanol as the major product; this reaction provides the first direct synthesis of 3-chromanols.

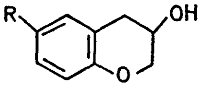
OXIDATIONS of olefins by thallium(III) salts have recently aroused much interest.[1] The products of such reactions have usually been glycol or carbonyl derivatives.



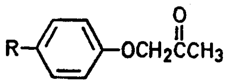
(1)

a; R = H c; R = MeO

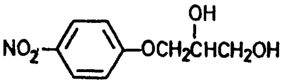
b; R = Me d; R = NO_2



(2)



(3)



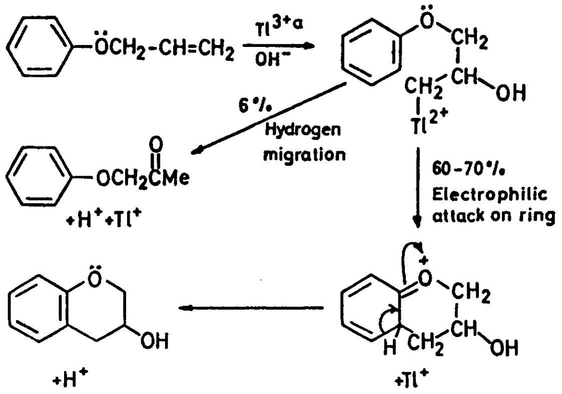
(4)

We have extended the range of olefins used to allyl phenyl ether and related compounds (**1**). Treatment of allyl phenyl ether (**1a**) (0·25 mol) with one litre of a well-stirred solution of thallium(III) sulphate (0·25 g ion Tl/l) in sulphuric acid (2·5M) was carried out at 40 °C and the reaction was complete after 40 min. Work-up of the mixture afforded a light brown oil which, on extraction with hot hexane, gave white crystals of 3-chromanol (**2a**) in 60—70% yield. Phenoxyacetone (**3a**) was also isolated in 6% yield. The unexpected formation of 3-chromanol may be rationalised as shown in the Scheme.

Allyl *p*-tolyl ether (**1b**) and allyl *p*-methoxyphenyl ether (**1c**) gave 6-methyl-3-chromanol (**2b**) and 6-methoxy-3-chromanol (**2c**), respectively, whilst allyl *p*-nitrophenyl ether (**1d**) was oxidised to a mixture of *p*-nitrophenoxyacetone (**3d**) and the diol (**4**) (see Table). The failure to produce a 3-chromanol in the last case can be explained by the fact that the position *ortho* to the ether group is no longer activated towards electrophilic attack.

Allyl phenyl ether (**1a**) was also successfully oxidised to 3-chromanol (**2a**) using thallium(III) perchlorate in 40%

perchloric acid and thallium(III) fluoroborate in 30% fluoroboric acid.



SCHEME

[a] The reactive species may be solvated or paired with sulphate.

This synthesis provides the most convenient route to 3-chromanol. Previous methods have involved either elaborate techniques[2] or multi-step synthesis.[3]

The structures of products were confirmed by comparison with authentic samples (i.r. and m.p.) and new compounds were identified by n.m.r., i.r., and elemental analysis.

TABLE[a]

Olefin	Reaction time[b] (min)	Product(s)	Yield (%)
(1a)	40	(2a)	60—70
		(3a)	6
(1b)	50	(2b)	41
(1c)	60	(2c)	20
(1d)	60	(3d)	35
		(4)	17

[a] All reactions were carried out at 40 °C. [b] Reaction was assumed to be complete when all the thallium(III) had been consumed.

We thank R. T. Jones for measurement and interpretation of the n.m.r. spectra.

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[1] A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Letters*, 1970, 5275.

[2] (a) W. Clark Still and D. J. Goldsmith, *J. Org. Chem.*, 1970, **35**, 2282; (b) B. S. Kirkiacharian and D. Raulais, *Bull. Soc. chim. France*, 1970, 1139.

[3] F. Baranton, G. Fontaine, and P. Maitte, *Bull. Soc. chim. France*, 1968, 4203.