

$\alpha$ -HALOGENOKETONES-X.<sup>1</sup> THE DEHYDROHALOGENATION OF o-ACYLOXY- $\alpha$ -BROMOACETOPHENONES TO  
CHROMONE EPOXIDES

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Chromone epoxides were obtained when 2-bromo-2'-acyloxy(or aroyloxy)acetophenones, trisubstituted at the 2-position, were dehydrobrominated in basic conditions. For example, 2'-acetoxy- $\alpha$ -bromodeoxybenzoin (1) reacted with aqueous methanolic sodium hydroxide to give 2-methyl-3-phenylchromone epoxide (3). This epoxide rearranged in acidic conditions to 3-hydroxy-2-methylene-3-phenylchromanone (6).

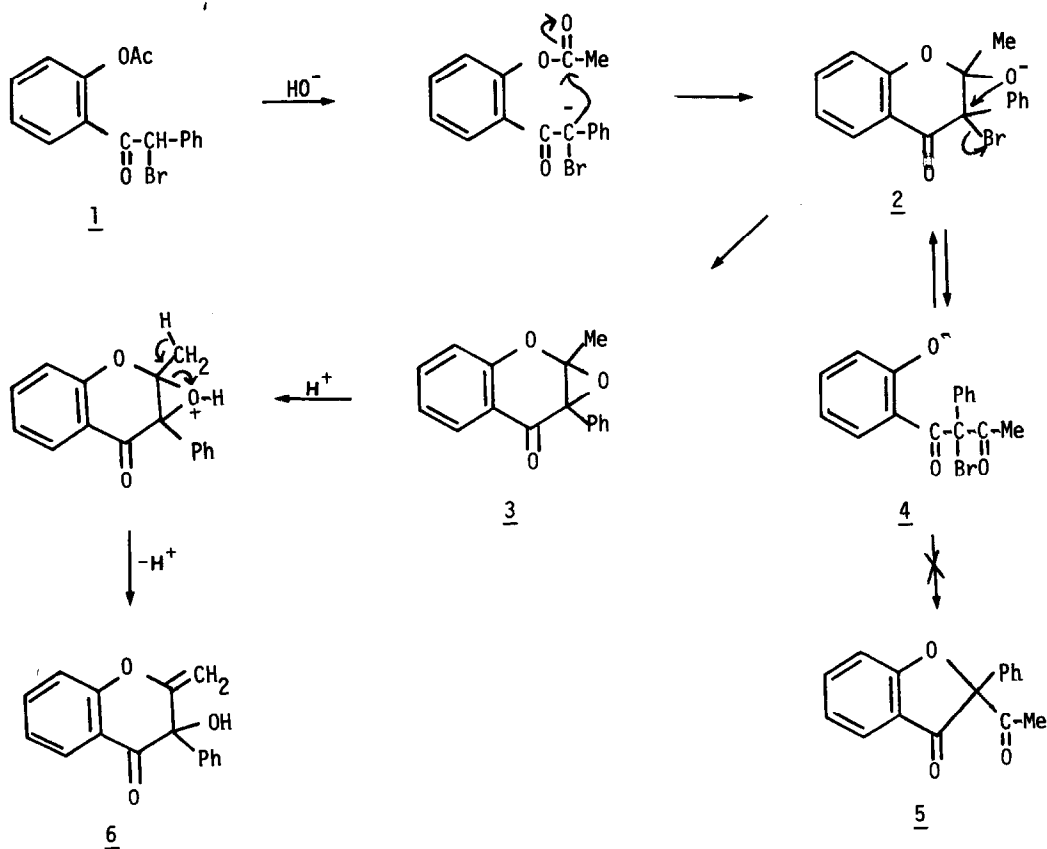
The formation of chromone epoxides (believed to be a previously unreported ring system) is probably initiated by a quasi Baker-Venkataraman rearrangement of the bromo-ester (1) to the oxyanion (2). The latter may be in equilibrium with the normal Baker-Venkataraman rearrangement product, the 1,3-diketone (4). In any case, because of the tertiary nature of the halogen in the 1,3-diketone, its normal substitution<sup>2</sup> to form a benzoylcoumaranone (5) - as in the Auwers synthesis<sup>3</sup> - is unlikely. Instead, addition to the carbonyl group to regenerate the oxyanion (2) would be expected. Elimination of bromide from the latter gives the chromone epoxide.

Satisfactory analyses were obtained for all new compounds. The chromone epoxide (3), m.p. 96-8°, has the <sup>1</sup>H n.m.r. spectrum ( $\delta$ ), in CDCl<sub>3</sub> with TMS as internal reference, 1.67 (s, Me), 7.46 (s, Ph), 8.04 (q, 5-H; J 8 and 3 Hz) and i.r. spectrum,  $\nu$ (KBr) 1682 cm<sup>-1</sup> (C=O). The <sup>1</sup>H n.m.r. spectrum of the methylene-chromanone (6), m.p. 152-3°, is 4.54 (s, OH), 5.30 (d, = CH; J 2Hz), 5.49 (d, = CH), 7.93 (q, 5-H; J 8 and 3 Hz); i.r. spectrum, 3450 cm<sup>-1</sup> (OH), 1684 cm<sup>-1</sup> (C=O).

The rearrangement of variously substituted chromone epoxides and the possibility of synthesising them from 2-halogeno-1,3-diketones are, at present, being studied.

## References

1. Part IX. D. J. Donnelly, J. A. Donnelly, and J. R. Keegan, Tetrahedron, **33**, 3289 (1977).
2. T. A. Geissman and A. Armen, J. Amer. Chem. Soc., **77**, 1623 (1955).
3. E. M. Philbin, W. I. A. O'Sullivan, and T. S. Wheeler, J. Chem. Soc., 4174 (1954).  
K. Auwers, Chem. Ber., **43**, 2192 (1910).



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