Phase Transfer Catalysed Double Carbonylation of Styrene Oxides

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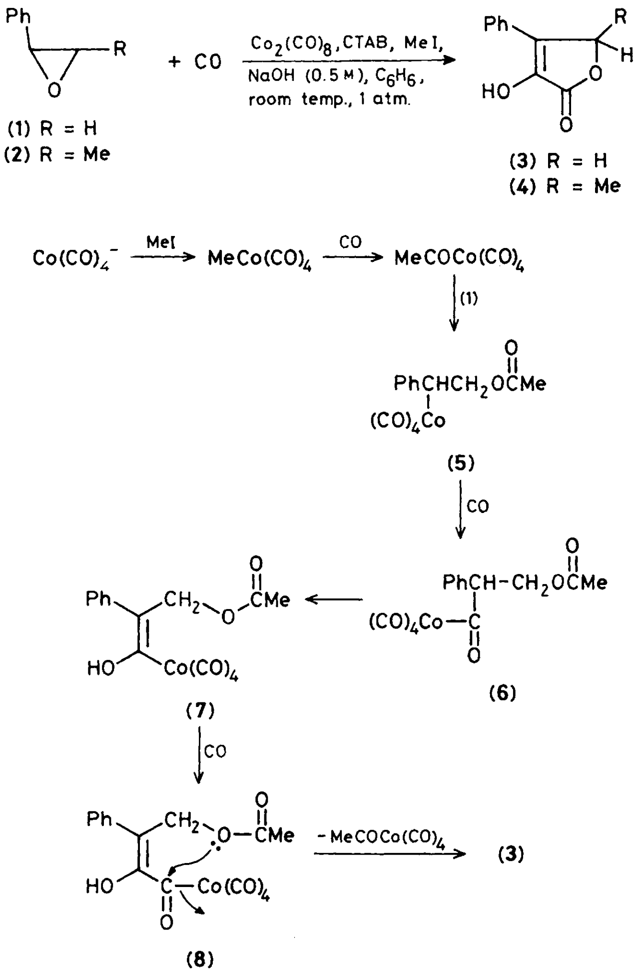
A novel double carbonylation of styrene oxides occurs on treatment of the heterocycle with carbon monoxide, methyl iodide, NaOH (0.5 M), C_6H_6, $Co_2(CO)_8$ as the metal catalyst, and cetyltrimethylammonium bromide as the phase transfer agent.

The successive incorporation of two molecules of carbon monoxide into appropriate organic substrates leads to products with adjacent carbonyl (or modified carbonyl) groups. Several of these compounds are of commercial importance (*e.g.*, α-keto acids). Phase transfer catalysis has proved to be an excellent technique for effecting double carbonylation reactions of halides using catalytic amounts of $Co_2(CO)_8$.[1—5] We now report the first examples of a mild, selective, cobalt- and phase transfer-promoted double carbonylation reaction of styrene oxides. The tetracarbonylcobalt anion, generated[1] by stirring a mixture of $Co_2(CO)_8$ (0.55 mmol, 187 mg) in benzene (50 ml), and



Scheme 1

NaOH (0.5 M, 50 ml) containing cetyltrimethylammonium bromide (CTAB) (0.55 mmol, 200 mg), was treated with an excess of MeI (64 mmol, 3 ml) while carbon monoxide was gently bubbled through at room temperature; styrene oxide (26 mmol, 3.12 g) was then added and the mixing continued overnight, to give the enol tautomer of 4,5-dihydro-4-phenylfuran-2,3-dione (**3**), in 65% selectivity (based on epoxide).† Similarly, the double carbonylated product (**4**) was obtained in 34% selectivity from β-methylstyrene oxide [2-methyl-3-phenyloxirane (**2**)]. The structures of the products were determined on the basis of analytical and spectral data,‡ and by comparison with properties of known materials.[6]

A possible mechanism for this novel transformation is outlined in Scheme 1, illustrated for (**1**). Addition of the *in situ* generated acetyltetracarbonylcobalt[7] to the epoxide gives a benzylcobalt complex (**5**) which on ligand migration to one of the four carbonyl carbons, followed by addition of carbon monoxide to the vacant co-ordination site, affords (**6**). Enolization of (**6**) to (**7**) may be the key step in the double carbonylation process, the insertion of the second molecule of carbon monoxide then occurring to give (**8**). Cyclization of the latter would then result in the regeneration of the acetylcarbonylcobalt, and the production of the enol of the furandione.§ The isolation of the latter compound provides support for the proposed participation of an enolized cobalt complex in the phase transfer catalysed double carbonylation of benzyl halides.[1,5] There is no evidence for the direct insertion of a second carbon monoxide into (**6**); indeed, α-methylstyrene oxide (2-methyl-2-phenyloxirane) does not undergo carbonylation under identical conditions to those described for (**1**) and (**2**) because the analogue of (**6**) would be non-enolizable. Furthermore, investigations on the mechanism of the homogeneous palladium catalysed double carbonylation of halides to α-keto amides (in the presence of secondary amines) indicate that the reaction does not occur *via* direct double carbonylation but by reductive elimination from a palladium intermediate bearing acyl and amide ligands.[8—10]

The base concentration is critical in the double carbonylation reaction since no reaction occurs either in 5 M NaOH or under neutral conditions. Such concentration effects may influence the distribution of intermediates [*e.g.*, $MeCOCo(CO)_4$] in the organic and aqueous phases, or the stability of the epoxide in the medium. It is noteworthy that no reaction is observed in the absence of the quaternary ammonium salt, thus in order to determine the true role of phase transfer conditions, the acetylcobalt complex was generated as usual, the two phases were separated, and then a stoicheiometric reaction of $MeCOCo(CO)_4$ with styrene oxide and carbon monoxide was effected under homogeneous conditions (benzene). The reaction was not selective and, in particular, none of the furandione (**3**) was detected, suggesting that the function of the phase transfer system is not simply to generate the acetylcarbonylcobalt but to promote enolization [*e.g.*, of (**6**)].

In conclusion, styrene oxides undergo a remarkable double carbonylation reaction under exceptionally mild conditions.

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† No glycol was found in the remaining solution.

‡ *Spectroscopic data:* (**3**) i.r. (ν CO) 1720 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) 5.15 (s, 2H, CH_2), 6.37 (s, 1H, OH), 7.55 (m, 5H, Ph); ^{13}C n.m.r. ($CDCl_3$) 68.20 (CH_2), 126.7 (benzylic carbon), 130.0 (C–OH), 126—136 (Ph carbons), 1709 (CO).(**4**) I.r. (ν CO) 1720 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) 1.58 (d, 3H, Me) 2.16 (s, 1H, OH), 5.47 (q, 1H, CH), 7.54 (m, 5H, Ph); ^{13}C n.m.r. ($CDCl_3$) 20.35 (Me), 76.90 (CH), 129.20 (C–OH), 130.0 (benzylic carbon), 128—136 (Ph carbons), 170.0 (CO).

§ The formation of the acetylcobalt anion prior to the epoxide introduction makes the opening of the styrene oxide by $Co(CO)_4^-$ most improbable. However, as suggested by a referee, MeI involvement in the cyclization step (**8**)→(**3**) cannot be entirely excluded at present.