Stereospecific Deoxygenation of Epoxides with Octacarbonyldicobalt

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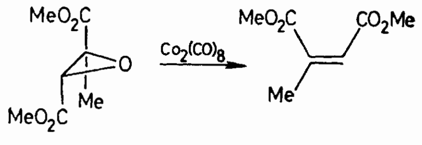
Summary A mild, high-yield, and in certain instances, highly stereospecific method for the deoxygenation, with inversion, of epoxy-esters using octacarbonyldicobalt is presented.

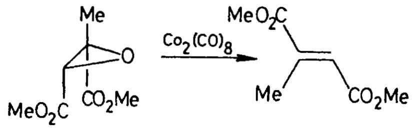
INTENSE interest exists in the development of new methods for the deoxygenation of epoxides and vicinal diols to olefins.[1] Since epoxides are often prepared with retention of stereochemistry from olefins, it would be valuable if the deoxygenation occurred with inversion of the epoxide stereochemistry. Inversion is a consequence of the *cis*-deoxygenation of *trans*-glycols[1d] and is a feature of the phosphide–phosphonium salt epoxide deoxygenation method of Vedejs.[1b]

Here, we present our results on a new, mild, stereospecific epoxide deoxygenating agent, $Co_2(CO)_8$, which causes inversion of the epoxide stereochemistry in the olefin product. This reaction is complementary to the

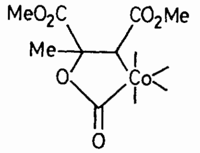
Vedejs method, since it may be used successfully on ester-bearing epoxides where the phosphide method[1b] meets difficulties. For this reason we have concentrated our initial efforts on the epoxy-esters; the phosphide–phosphonium salt method appears to be quite successful with other substituted epoxides.



(I) (II)



(III) (IV)



(V)

Thus, treatment of *cis*-dimethyl epoxymethylsuccinate (I) with $Co_2(CO)_8$ (0·147 equiv.), neat for 18 h at room temperature yields 95% of dimethyl mesaconate (II). Only 3% of citraconate and 2% starting epoxide were recovered from this reaction. Under the same conditions *trans*-dimethyl epoxymethylsuccinate (III) yields 99% of dimethyl citraconate (IV) contaminated with 1% of dimethyl mesaconate.

Dependence on the amount of $Co_2(CO)_8$ is interesting. If relatively large amounts are used, deoxygenation is faster, but less stereospecific. For example, an equimolar amount of $Co_2(CO)_8$ reacts completely in 5 h with the *cis*-diester (I), but the ratio of *trans*- to *cis*-olefin product falls to 80:20. The olefin products are stable to the reaction conditions, and if the reaction is followed by g.l.c., no isomerization of starting epoxide is observed. This suggests that an intermediate, which would ordinarily lead to inversion, is being intercepted and the reaction diverted to products of retained stereochemistry. On this basis and that of the stoicheiometry we tentatively suggest that an intermediate cobalt heterocycle such as (V) may be important in this reaction. Those molecules not reaching an intermediate such as (V), or its mechanistic equivalent, would be led to product with retained stereochemistry.

The reaction may also depend upon the presence of conjugating or electron-withdrawing groups for activation. Thus reaction of methyl epoxycrotonate with $Co_2(CO)_8$ results in a slower deoxygenation (24 h) to a 50:50 mixture of *cis*- and *trans*-methyl crotonates. However, if $Co_2(CO)_8$ is replaced by $NaCo(CO)_4$ an improvement in stereoselectivity is observed, and a 70:30 *cis–trans*-mixture of crotonates is obtained. In both reactions the deoxygenation is quantitative, but the $NaCo(CO)_4$ reaction is approximately five-fold slower than the $Co_2(CO)_8$ reaction.

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[1] (a) D. L. J. Clive and C. V. Denyer, *J.C.S. Chem. Comm.*, **1973**, 253; (b) E. Vedejs and P. L. Fuchs, *J. Amer. Chem. Soc.*, 1973, **95**, 822; 1971, **93**, 4070; (c) T. Hiyama and H. Nozaki, *Bull. Chem. Soc. Japan*, 1973, **46**, 2248; (d) E. J. Corey and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1973, **85**, 2677.