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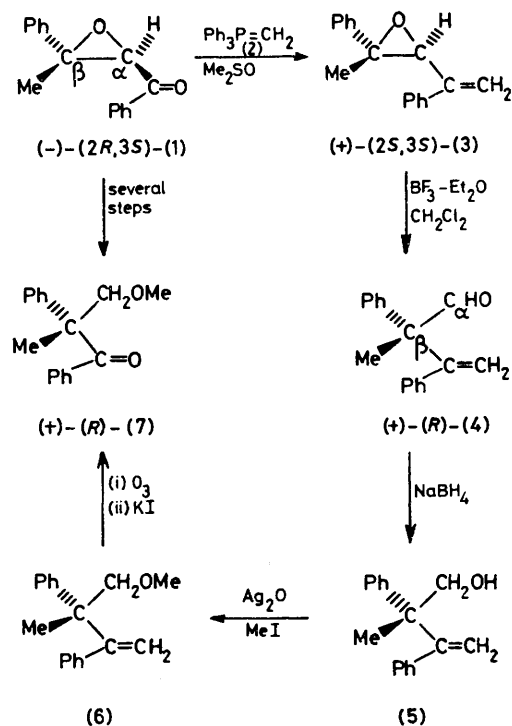
## Stereochemistry of Concerted 1,2-Vinyl Migration to a Developing Carbenium-ion Centre

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**Summary** The first example of the stereochemistry of vinyl migration employing an optically active substrate is reported; the parallel behaviour between 1,2-migration of a vinyl group and a carbonyl group, under otherwise identical conditions, provides additional evidence for the concept of neighbouring group participation at carbonyl carbon in 1,2-acyl migrations.

1,2-VINYL migration in a vinyl substituted epoxide is a concerted rearrangement that occurs with inversion of configuration at C<sub>β</sub> without loss of optical activity. A number of investigations of concerted 1,2-migrations to adjacent developing positive centres have provided much evidence for neighbouring group participation by carbon-carbon multiple bonds.<sup>1</sup> The best known of these studies was on phenonium ion involvements in solvolytic and deamination reactions.<sup>2,3</sup> More recently, we have provided the first example of neighbouring group participation by a carbonyl group, at carbon, in our stereochemical studies on 1,2-acyl migration.<sup>4</sup> Ethoxycarbonyl migration in a glycidic ester<sup>4a</sup> and benzoyl migration<sup>4b</sup> in the structurally related dypnone oxide (1) occurs stereospecifically with inversion of configuration at the migration terminus. Identical stereochemical behaviour was noted in the silver catalysed 1,2-benzoyl rearrangement of a pair of diastereomerically related chlorohydrins.† We now report a stereospecific migration of a vinyl group to a chiral centre in a related pinacolic type rearrangement that proceeds by an analogous pathway without a detectable loss of optical activity (Scheme).



SCHEME

† Benzoyl migration in both (-)-(2R,3R)- and (+)-(2R,3S)-3-chloro-2-hydroxy-1,3-diphenylbutan-1-one proceeds with complete stereospecificity in nonpolar solvents. Migration occurs through the least stable conformer where the departure of the leaving chlorine can be assisted by the carbonyl carbon as depicted in (8). J. M. Domagala and R. D. Bach, *J. Amer. Chem. Soc.*, submitted for publication.

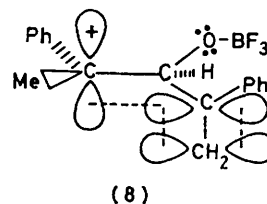
We chose the vinyl-substituted epoxide (**3**) as substrate since this provides a unique opportunity to ascertain the stereochemistry of vinyl migration to a developing homoallylic cationic centre. (+)-(2*S*,3*S*)-2,4-Diphenyl-1,3-epoxypent-4-ene (**3**),  $[\alpha]_D^{25}$  6.0° (*c* 2.76, CHCl<sub>3</sub>), was prepared by the reaction of (**1**),<sup>4b</sup>  $[\alpha]_D^{25}$  -6.2° (*c* 2.25, CHCl<sub>3</sub>), with methylenetriphenylphosphorane in dry Me<sub>2</sub>SO for 30 min at 60 °C; n.m.r. (CDCl<sub>3</sub>) δ 7.7—7.1 (m, 10H), 5.72 (s, 1H), 5.28 (s, 1H), 3.50 (s, 1H), and 1.63 (s, 3H).

The rearrangement of (**3**) was carried out at 0 °C in CH<sub>2</sub>Cl<sub>2</sub> with BF<sub>3</sub>·Et<sub>2</sub>O. After 30 s the reaction was quenched by addition of H<sub>2</sub>O affording (+)-(R)-2-methyl-2,3-diphenylbut-3-enal (**4**) (99%),  $[\alpha]_D^{25}$  9.8° (*c* 1.70, CHCl<sub>3</sub>); n.m.r. (CDCl<sub>3</sub>) δ 9.82 (s, 1H), 7.4—6.8 (m, 10H), 5.27 (s, 1H), 5.18 (s, 1H), and 1.62 (s, 3H); m.p. 126—127 °C (2,4-dinitrophenylhydrazone).

The absolute configuration and optical purity of the product (**4**) were established by its conversion into the oxo-ether (+)-(R)-(**7**) of known stereochemistry.<sup>4b,5</sup> Reduction of (+)-(**4**) with NaBH<sub>4</sub> in absolute ethanol gave the alcohol (**5**) (98%) which was converted into the methyl ether (**6**) (91%) by the action of Ag<sub>2</sub>O in refluxing methyl iodide. Ozonolysis of the double bond in (**6**) in anhydrous methanol at -78 °C gave (+)-(R)-2-methoxymethyl-1,2-diphenylpropan-1-one (**7**) (96%);  $[\alpha]_D^{25}$  5.0° (*c* 1.64, CHCl<sub>3</sub>). The chiral centre in (+)-(**7**) has the *R* configuration which necessitates a vinyl migration with inversion at the oxiran carbon. The transformation of (**1**) to (**7**) was achieved with an overall stereospecificity of 98%.<sup>†</sup> These data are consistent with a concerted migration in the absence of a carbenium ion intermediate. Probably carbonyl formation at C<sub>α</sub> precludes formation of a discrete cyclopropylcarbinyl

intermediate which accounts for the absence of competing homoallylic-homoallylic rearrangement in this system. Carbenium ion intermediates have been rigorously excluded in comparable carbonyl migrations.<sup>4</sup>

The transition state for a concerted 1,2-shift may be stabilized by bonding interactions of the migrating substituent with the adjacent reaction centre as shown in (**8**). We suggest an unsymmetrically bridged transition state (**8**) with participation by the neighbouring π-bond in explanation of the rapid rate of this concerted rearrangement.



In conclusion, we have provided a demonstration of the parallel behaviour of a vinyl and carbonyl group that provides corroborative evidence for our earlier suggestion of neighbouring group participation at carbonyl carbon in acyl migrations.

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<sup>†</sup> The optical purity of (**1**) is 4.2% based upon a reported<sup>4b</sup> rotation of 147.2° (CHCl<sub>3</sub>). Compound (**7**) is 4.1% optically pure based upon a maximum rotation of 122.0°. In a duplicate experiment the overall stereospecificity was greater than 100%. Compounds (**3**), (**4**), and (**7**) gave satisfactory elemental analyses.

<sup>1</sup> B. Capon and S. P. McManus, 'Neighboring Group Participation,' Vol. 1, Plenum Press, New York, 1976.

<sup>2</sup> D. J. Cram, *J. Amer. Chem. Soc.*, 1949, **71**, 3863; D. J. Cram and J. E. McCarty, *ibid.*, 1957, **79**, 2866.

<sup>3</sup> C. J. Collins, *Accounts Chem. Res.*, 1971, **4**, 315.

<sup>4</sup> (a) J. M. Domagala, R. D. Bach, and J. Wemple, *J. Amer. Chem. Soc.*, 1976, **98**, 1975; (b) J. M. Domagala and R. D. Bach, *ibid.*, 1978, **100**, 1605.