

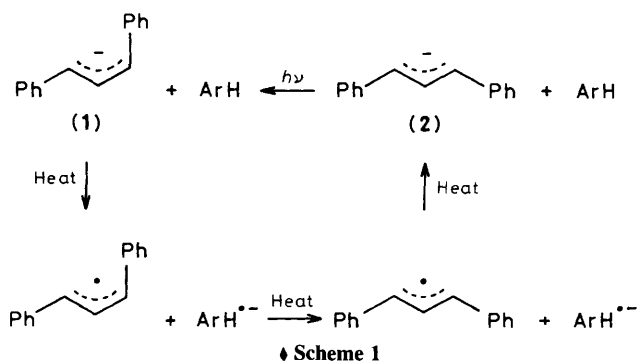
A Single Electron Transfer Mechanism for Thermal *cis* to *trans* Isomerisation of Delocalised Organic Anions

Richard J. Bushby* and Myron P. Tytko

Department of Organic Chemistry, The University, Leeds LS2 9JT, U.K.

The thermal isomerisation of *cis,trans*-diphenyl allyl anion (1) to its *trans,trans*-conformer (2) can be catalysed by electron acceptors.

A solution of the lithium salt of 1,3-diphenylallyl anion in tetrahydrofuran at 0 °C consists almost exclusively of solvent separated ion pairs and roughly 91% of the *trans,trans*-conformer (2) and 9% of the *cis,trans*-conformer (1).^{1,2} When it is exposed to light of a suitable wavelength most of the *trans,trans*- is converted into the *cis,trans*-form and on removing the source of illumination there is a first order return to equilibrium.^{2,3} This method of generating conformer (1) which is due to Young³ is simpler than that employed by Boche¹ but, strangely, it is limited to certain solvents. For example it is difficult or impossible to observe photogeneration of the *cis,trans*-conformer in liquid ammonia.² When using this method we experienced difficulty in obtaining reproducible kinetics for the thermal return to equilibrium in tetrahydrofuran solution. This was traced to the presence of diphenylpropene as an impurity. This we believe catalyses the isomerisation by acting as a single electron acceptor. Indeed we have shown that other aromatic hydrocarbons such as anthracene and phenanthrene catalyse the isomerisation. For the catalysed part of the reaction second order kinetics are obtained, rate = $k_2[\text{ArH}][\text{(1)}]$, k_2 (anthracene) = 0.021 l mol⁻¹ sec⁻¹ (227 K), k_2 (phenanthrene) = 0.0171 mol⁻¹ sec⁻¹ (227 K). For a series of aromatic hydrocarbons k_2 correlates with the energy of the half wave reduction potential (or the energy of the lowest unoccupied molecular orbital) following the order anthracene > phenanthrene > triphenylene > biphenyl.⁴ The simplest mechanism to account for these observations is that shown in Scheme 1 where it is assumed that the initial electron transfer is rate determining. It is known that the energy barrier to *cis* → *trans* isomerisation in the radical is much less than that in the anion.^{1,3,5} The single electron transfer (SET) mechanism also provides one explanation for the difficulty experienced in photogeneration of conformer (1) in ammonia since easy production of solvated electrons in this solvent would provide for rapid relaxation to the *trans,trans*-form. The ease with which they are ionised



means that SET mechanisms are particularly important for carbanions⁶ and although we believe this is the first case where SET has been suggested as a mechanism for their *cis* → *trans* isomerisation⁷ it is quite probable that such isomerisation mechanisms are widespread.

We thank the S.E.R.C. for financial support.

Received, 18th September 1985; Com. 1366

References

- 1 G. Boche and D. R. Schneider, *Tetrahedron Lett.*, 1976, 3657.
- 2 R. J. Bushby, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1419.
- 3 H. M. Parkes and R. N. Young, *J. Chem. Soc., Perkin Trans. 2*, 1978, 249.
- 4 A. W. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, Table 7.1.
- 5 G. Boche and D. R. Schneider, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 869.
- 6 E. C. Ashby, *Pure Appl. Chem.*, 1980, **52**, 545; W. Kaim, *Acc. Chem. Res.*, 1985, **18**, 160.
- 7 R. J. Bushby and G. J. Ferber, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1688.