An Instance of *trans*-Hydrogen Addition in Catalytic Homogeneous Hydrogenation

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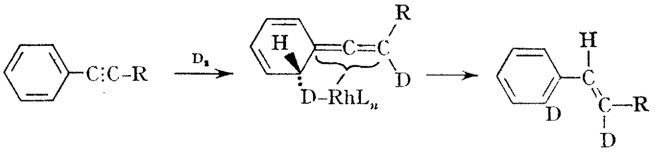
Summary Reduction of diphenylacetylene with deuterium gas using the py_3RhCl_3–$Me_2N{\cdot}CHO$–$NaBH_4$ catalyst system is found to involve deuterium incorporation at the *ortho*-position of the phenyl group of the product, *trans*-stilbene, considered to arise by a mechanism of *ortho*-deuteriation accompanied by 1,3-hydride shift.

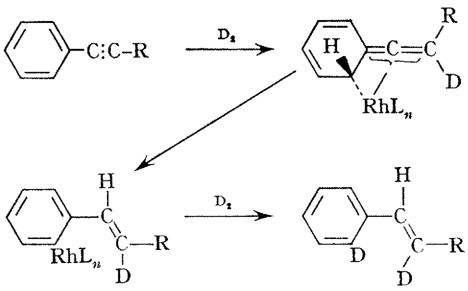
HOMOGENEOUSLY-CATALYSED hydrogenation appears to be generally characterised by *cis*-hydrogen addition.[1] The following examples of catalysis by the –$Me_2N{\cdot}CHO$–$NaBH_4$ system[2] were found to conform to this pattern: dimethyl acetylenedicarboxylate–dimethyl maleate, butyne-1,4-diol –*cis*-but-2-ene-1,4-diol. With deuterium, maleic and fumaric acids gave, respectively, *meso-* and (±)-1,2-dideuteriosuccinic acid.[3] Diphenylacetylene, however, was found to be exceptional in giving *trans*-stilbene as sole product. *cis*-Stilbene was found to be stable to stereomutation by this catalyst system.

trans-Hydrogen addition by intramolecular hydrogen transfer within a discrete molecular complex is difficult to formulate. A somewhat analogous difficulty arises in heterogeneous catalysis, in the case of hydrogenolysis at a benzyl centre, which, at palladium, occurs with stereochemical inversion.[4] Both these instances are concerned with hydrogen addition α to a phenyl group, and we were led to consider that the phenyl group is in fact the primary hydrogen acceptor, the isolated product arising by a hydride-transfer rearrangement.

Schematically such a reaction sequence may be represented:



However, hydrogen migration may precede *ortho*-deuteriation:



A process of this type which involves *cis*-addition of deuterium, and migration of hydrogen on the remote face of the molecule, should lead to deuterium incorporation at the *ortho*-position of the phenyl group, and in the vinyl position in equal amount. The suggested *ortho*-deuteriation has established precedents.[5] In terms of the Woodward–Hoffmann rules a 1,3-hydride shift in a concerted process should be antarafacial,[6] but there is good evidence that in metal-complexed systems these symmetry rules no longer apply, and that a suprafacial 1,3-shift is permitted.[7]

The *trans*-stilbene obtained from deuteriation of diphenylacetylene (0·2 M) with py_3RhCl_3–$NaBH_4$ (0·01 M) in $Me_2N{\cdot}CHO$ gave P^+ $m/e = 182$ ($C_{14}H_{10}D_2$). From n.m.r. absorption in deuteriobenzene solution *ortho*-protons may be distinguished from *meta*- and *para*-protons.[8] Comparison of the n.m.r. spectra in deuteriobenzene of *trans*-stilbene with the deuterio-*trans*-stilbene product showed a clear reduction of signal strength for *ortho*-protons (τ 2·5—2·7) in comparison with the signal strength for *meta*- and *para*-protons (τ 2·7—2·9). Also the vinylic proton signal (2·9) was found to be about half the intensity observed with *trans*-stilbene.

These results are consistent with the suggested mechanism of 1,3-hydride shift accompanied by *ortho*-deuteriation. *ortho*-Hydrogen exchange independently of deuterium addition to the triple bond would lead to a rather different pattern of deuterium incorporation, and would also leave the stereochemistry of the reaction unexplained.

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[1] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1771; F. H. Jardine, J. H. Osborn, and G. Wilkinson, *ibid.*, 1967, 1574; I. Jardine and F. J. McQuillin, *Tetrahedron Letters*, 1966, 4871.

[2] I. Jardine and F. J. McQuillin, *Chem. Comm.*, 1969, 477.

[3] C. R. Childs and K. Bloch, *J. Org. Chem.*, 1961, **26**, 1630.

[4] A. M. Khan, F. J. McQuillin, and I. Jardine, *J. Chem. Soc.* (*C*), 1967, 136; S. Mitsui, Y. Kudo, and M. Kobayashi, *Tetrahedron*, 1969, **25**, 1921.

[5] *Cf.* M. A. Bennett and D. L. Milner, *Chem. Comm.*, 1967, 581; G. W. Parshall, *J. Amer. Chem. Soc.*, 1969, **90**, 1669.

[6] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 2511.

[7] F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, 1967, **89**, 2484; F. G. Cowherd and J. L. von Rosenberg, *ibid.*, 1969, **91**, 2157.

[8] G. W. Parshall, *J. Amer. Chem. Soc.*, 1968, **90**, 1669.