

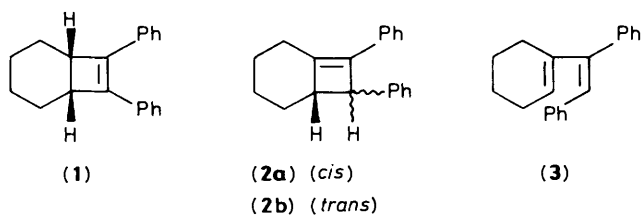
Surface Photochemistry: a [1,3] Sigmatropic Hydrogen Shift mediated by CdS

Paul de Mayo* and Grazyna Wenska

Photochemistry Unit, Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

Excitation of CdS in the presence of 7,8-diphenylbicyclo[4.2.0]oct-7-ene gave the cation radical of the latter which underwent a reversible [1,3] sigmatropic hydrogen shift; this is the first such observation in a radical cation.

The successful application of semiconductors to photoinduce organic reactions has been demonstrated recently. The reactions reported, other than oxidation and reduction, include: the dimerization of phenyl vinyl ether^{1,2} and *N*-vinylcarbazole;³ the cycloreversion of a cage molecule,⁴ anthracene,¹ and quinolone dimers;⁵ the valence isomerization of hexamethyl Dewar benzene;^{5,6} and the *cis-trans* isomerization of alkenes.^{7,8} The reactions were shown to proceed through radical cations generated by electron transfer from organic substrates to the photogenerated holes on the semiconductor. Theoretical calculations of the reaction pathway for some representative pericyclic processes (Diels-Alder, alkene cycloaddition, and the Cope rearrangement) have predicted that prior electron transfer to form radical



cations should facilitate these reactions by lowering the activation energies for the transition states.⁹ The same conclusion concerning the specific case of electrocyclic reactions has emerged from mass spectrometric studies.¹⁰ We report here the first observation of a symmetry-forbidden (if

'concerted') suprafacial [1,3] sigmatropic[†] H shift in a radical cation, the interconversion of bicyclo[4.2.0]octenes (1) and (2a), mediated by cadmium sulphide.[‡]

Irradiation ($\lambda > 420$ nm) of a degassed suspension of CdS in CH_2Cl_2 containing 7,8-diphenylbicyclo[4.2.0]oct-7-ene (1)¹² ($c 7.7 \times 10^{-3}$ M) gave (2a) as the major (>80%) product. The reaction was highly stereoselective (>90%); only one isomer could be detected. In the absence of light or CdS (1) was recovered quantitatively. The reaction could be quenched[§] by 1,2,4-trimethoxybenzene [$E_1^{\text{ox}} = 1.12$ V vs. standard calomel electrode (s.c.e.)]¹⁴ and a plot of ϕ^0/ϕ vs. the concentration of the quencher (Stern-Volmer) was linear ($r = 0.968$) with a slope of $585 \text{ dm}^3 \text{ mol}^{-1}$.

The structure of the product (2a) was established on the basis of spectral data (¹H, ¹³C n.m.r., mass, u.v.). *cis*-Stereochemistry was assigned by a comparison of chemical shifts and coupling constants of the cyclobutene ring protons in (2a) with those of (2b) available [together with (2a)] by mild treatment of (1) with acid (1 M $\text{Cl}_3\text{CCO}_2\text{H}$ in benzene at room temperature). An additional proof for the structure of (2a) is its thermal (sealed tube, 160 °C, 3 h) isomerization to α -(cyclohex-1-enyl)stilbene (3).

CdS-mediated rearrangement (1) \rightarrow (2a) was, however, an inefficient reaction (3% conv., 4.5 h irradiation, 1 kW lamp). The inefficiency may, in part, be attributed to a fast back

reaction, (2a) \rightarrow (1). Indeed, irradiation ($\gamma > 420$ nm) of (2a) ($c 3.5 \times 10^{-3}$ M, CH_2Cl_2 , degassed sample) in the presence of CdS resulted in the formation of (1). The initial rate of this reaction was several times faster than the conversion of (1) \rightarrow (2a). Again, both light and semiconductor are required for the reaction to occur.

G. W. is on leave from A. Mickiewicz University, Poznan, Poland.

Received, 3rd June 1986; Com. 754

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[†] The only previously reported sigmatropic reactions were an idiosyncratic zeolite-induced Cope rearrangement,¹¹ and the rearrangement of a methylenecyclopropane derivative.⁵

[‡] The use of excited 9,10-dicyanoanthracene as an electron acceptor did not lead to the conversion of (1) into (2a), though it is an adequate oxidizing agent. Instead, the sensitizer was consumed and two thermally unstable adducts were isolated.

[§] Presumably the oxidation potential of (1) is close to that of *cis*-stilbene (1.58 V vs. s.c.e.¹³).