Tetrahedron Vol. 43, No. 7, pp. 1661 to 1670, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00
Pergamon Journals Ltd.

SURFACE PHOTOCHEMISTRY; A "SYMMETRY FORBIDDEN" [1,3] SIGMATROPIC HYDROGEN SHIFT MEDIATED BY CdS.[1]

PAUL de MAYO* AND GRAZYNA WENSKA[2]

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

(*Received in UK* 16 *February* 1987)

Abstract: Excitation of CdS in the absence of oxygen in the presence of cyclic derivatives of diphenylcyclobutene gave the cation radical of the latter which underwent a reversible double bond migration. The structures of the products were established on the basis of spectral data (^1H, ^{13}C NMR, MS, UV). Tests were performed to show that the reaction proceeds, at least in part, intramolecularly, and, therefore, represents the first example of a suprafacial [1,3] sigmatropic hydrogen shift via a radical cation. This suprafacial pathway is symmetry forbidden in closed shell systems. Oxidation products were isolated when the irradiation was performed in an aerated system. The use of excited 9,10-dicyanoanthracene as an electron acceptor did not lead to the expected products; instead the sensitizer was consumed and two thermally unstable adducts were isolated. Their formation could be quenched by 1,2,4-trimethoxybenzene.

INTRODUCTION

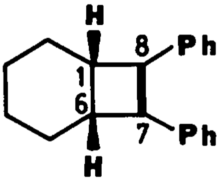
The successful application of semiconductors to photoinduce organic reactions has been demonstrated recently. The reactions reported, other than oxidation and reduction, include: the dimerization of phenyl vinyl ether[3,4] and N-vinylcarbazole[5]; the cycloreversion of a cage molecule[6], of anthracene[3] and of quinolone dimers[7], the valence isomerization of hexamethyl Dewar benzene[7,8] and the cis-trans isomerization of olefins[9,10]. In these reactions the involvement of radical cations formed by electron transfer from organic substrates to the holes photogenerated in the valence band of semiconductor has been demonstrated.

Theoretical calculations of the reaction pathway for some representative pericyclic processes (Diels-Alder, olefin 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 their transitions states[11]. The same conclusion concerning the specific case of electrocyclic reactions has emerged from mass spectroscopic studies[12]. We report here the results of our study concerning the semiconductor mediated photoreactions of diphenylcyclobutenes 1 which, in the absence of oxygen, undergo a reversible [1,3] sigmatropic hydrogen shift [13]. Part of this work has been described[15].

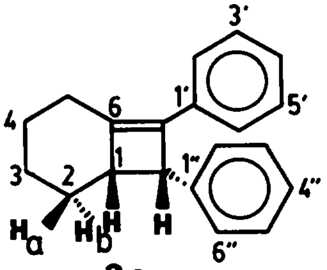
RESULTS AND DISCUSSION

CdS photoinduced reactions.

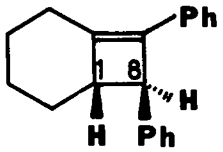
Irradiation (λ>420 nm) of a degassed suspension of CdS in CH_2Cl_2 containing cis-fused 7,8-diphenyl bicyclo[4.2.0]oct-7-ene[16], **1a**, gave **2a** as the major product (Table). Both light and semiconductor were required for reaction. The



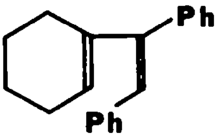
1a



2a



3a

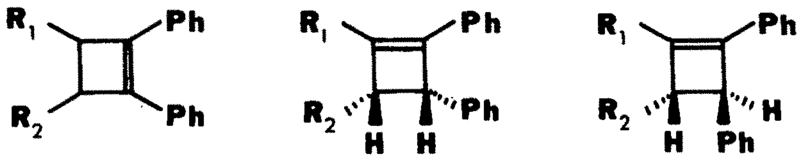


4

structure of the product **2a** was established on the basis of spectral data (NMR, UV, MS). Cis stereochemistry was assigned by a comparison of chemical shifts and coupling constants of the cyclobutene ring protons in **2a** with those of two isomeric 7,8-bicyclo[4.2.0]oct-6-enes: **2a** (cis) and **3a** (trans) obtained by acid catalyzed rearrangement of **1a**. Both cis and trans isomers were found to have the same elemental composition as the starting material **1a**, but they both lacked the characteristic UV absorption of the stilbene chromophore (see Experimental). ^1H NMR spectra of **2a** and **3a** showed only a multiplet, corresponding to aromatic protons, in the low field region. In the ^1H NMR spectrum of **2a** a doublet of doublets at δ 4.39 ppm and a multiplet at ca. δ 2.80 ppm were ascribed to H_8 and H_1, respectively. A double resonance experiment revealed that a benzylic proton H_8 is coupled to vicinal H_1($J_{H_1H_8}$ = 5.1Hz) and most probably to H_{2a} by long range coupling ($J_{H_8H_{2a}}$ = 3.0 Hz)[17]. The H_8 and H_1 protons in the trans isomer **3a** give rise to a broad doublet[19] at δ 3.75 ppm and to a multiplet centered at δ ca. 2.30 ppm, respectively. The cyclobutenyl H_1 is shielded by the adjacent cis phenyl ring and appears at higher field as compared with **2a**. Irradiation of the multiplet at δ ca. 2.30 ppm causes the doublet at δ 3.75 ppm to collapse to a singlet. First order analysis of the spectrum of **3a** gives $J_{H_1H_8}$ = 2.9 Hz. These assignments are in agreement with those made for 1,3-diphenylcyclobutene,[20a] (cyclobutenyl H cis to phenyl ring δ = 2.56 ppm; H trans to phenyl ring δ = 3.22 ppm, $J_{H_3H_4}$ cis = 4.9 Hz, $J_{H_3H_4}$ trans = 1.9 Hz), and 3-phenylcyclobutene[20b]. The ^{13}C NMR spectrum of **2a** fits the assigned structure well, and a DEPT experiment showed the presence of the required number of quaternary, tertiary and secondary carbons.

Additional proof for the structure of **2a** was obtained by its thermal isomerization to α-(cyclohexen-1-yl) stilbene **4**. Conrotatory ring opening of **2a** is expected to give the trans isomer, and a trans stereochemistry of the product derived from **2a** was indicated clearly by ^1H NMR. The chemical shifts of vinyl protons and the appearance of the aromatic proton signal have been reported to be of diagnostic value in differentiation of cis and trans isomers of 1,2-diphenylbuta1,3-diene.[21]

Irradiation of a CdS suspension in CH_2Cl_2 containing cis-fused 8,9-diphenylbicyclo[5.2.0]non-8-ene[16] **1b** gave **2b** as the sole product (Table). The ^1H NMR spectrum of **2b** is compatible with the assigned structure. The benzylic H and the remaining cyclobutenyl H appeared at δ 4.27 and 3.05 ppm, respectively, both as multiplets. Double resonance again showed the presence of long range coupling ($^4J_{HH}$ and/or $^5J_{HH}$) with ϕC*H*. Irradiation at ca. 3.05 ppm simplified the benzylic H signal significantly. When the multiplet at δ ca. 2.7 ppm was irradiated the



R_1-R_2:$(CH_2)_5$	**1b**	**2b**	**3b**
R_1-R_2:$(CH_2)_3$-O	**1c**	**2c**	
R_1=R_2=H	**1d**		

ϕCH signal collapsed to a doublet. The coupling constant thus determined, J_{HH} = 5.2 Hz, as well as the chemical shifts of the cyclobutenyl protons are in agreement with a cis stereochemistry[20].

CdS photocatalyzed reactions of **1a** and **1b** proceeded with a high degree of stereoselectivity. Neither for **1a** nor for **1b** could the trans isomers, **3a** and **3b**, be isolated from the solutions irradiated in the presence of the semiconductor. On the other hand, both **2a** and **3a**, in the ratio 2:1, (determined by ^{1}H NMR spectroscopy by the integration of ϕCH cis and trans isomer signals at δ 4.39 and 3.75 ppm) are formed by acid catalyzed rearrangement of **1a**. Similarly, the doublet at δ 3.74 ppm, ascribed, by an analogy with **3a**, to the trans isomer **3b**, appeared in the ^{1}H NMR spectrum of the mixture obtained after treatment of **1b** with 2.6 M trifluoroacetic acid.

The CdS mediated rearrangement **1**→**2** is, however, an inefficient reaction (Table). The inefficiency may, in part, be attributed to a fast back reaction **2**→**1**. Irradiation of **2a** and **2b** in the presence of CdS was, indeed, found to afford **1a** and **1b**, respectively. The structures of the products were established by a comparison with authentic samples. The ^{1}H NMR spectrum of the product obtained from **2a** was identical with that reported for cis-fused 7,8-diphenyl bicyclo[4.2.0]oct-7-ene (**1a**)[16]. As shown in Table, under comparable conditions, the initial rate of these reactions was faster than the conversion of **1**→**2**.

Table

CdS mediated photoreactions[a] of 1 and 2

Substrate ([c] × 10^2M)	Condition	irr. time (h)	conversion (%)	product (yield %)[b]
1a (0.77)	degassed	4.5	3	**2a** (80)
2a (0.77)	degassed	4.5	21	**1a** (90)
1b (0.88)	degassed	7	11	**2b** (92)
2b (0.36)	degassed	5.5	29	**1b** (70)
1c (2.30)	degassed	11	<1	
1c (2.30)	air	4.5	17	not identified
1d (3.10)	degassed	30	0	
1d (3.10)	air	17.5	30	5 (65) + 6 (35)

[a] all irradiation at λ>420 nm.
[b] GC determined, calcd. on the basis of reacted substrate

Essentially no reaction was observed when degassed samples **1c** and **1d** were irradiated in the presence of CdS for 11 h and 30 h respectively. The lack of observed chemistry in the absence of oxygen may be attributed to the rapid quenching of the initially formed radical cations by photogenerated electrons in the conduction band of semiconductor. Oxygen is known to prevent this process by capturing electrons to produce surface-bound $O_2^{\overline{\cdot}}$ and possibly by modification of band bending[4]. When **1c** and **1d** were subjected to CdS photocatalyzed reaction in the presence of atmospheric air the substrates disappeared faster (Table), but the isomeric cyclobutens (e.g. **2c**) were not isolated. The mixture of products obtained from **1c** after SiO_2 chromatography showed in the IR spectrum (CCl_4) intense carbonyl stretching bands in the 1750-1660 cm^{-1} region. The mere presence of cyclohexanone and/or cyclobutanone (ν_{CO}>1715 cm^{-1}) suggests that double bond migration in **1c** may have occurred. Electron transfer oxidation of **1c** should lead, by analogy with stilbene,[22] to 2,3-dibenzoyl-3,4,5,6-tetrahydro-2H pyran (ν_{CO} = 1685, 1670 cm^{-1})[16]. No indication of double bond migration was found, however, in the case of 1,2-diphenylcyclobutene **1d**. Here two oxidation products: 1,2-dibenzoylethane **5**[23] and 1-phenylcyclopropyl phenyl ketone **6**[24], in the ratio 2:1, (GC determined) were formed. They were separated by SiO_2 chromatography and identified by a comparison with authentic, synthesized samples. The structure of the products are as expected for oxidation of stilbene derivatives[22]. Product **6** is presumably formed from 1,2-diphenylcyclobutane epoxide: cyclobutane epoxides are known to undergo thermal ring contraction[25].

The CdS mediated formation of **2a** could be quenched by 1,2,4-trimethoxybenzene ($E^{ox}_{1/2}$ = 1.12 V vs. SCE)[26] and the plot of $\phi°/\phi$ (relative quantum yields without and with the quencher present) vs. concentration of the quencher is presented in Fig. 1.

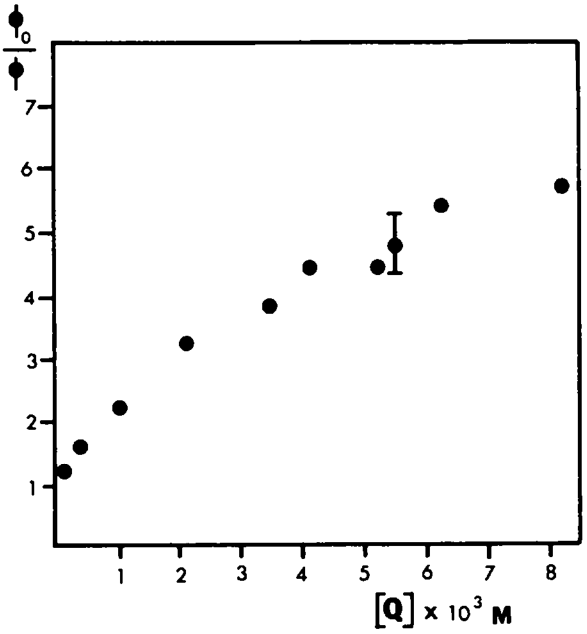


Fig. 1 Quenching of **2a** formation by 1,2,4-trimethoxybenzene.

[**1a**] = 2.3 x 10^{-2} M; CdS (100mg)/in CH_2Cl_2 (5mL); degassed sample.

Quenching of the reaction by an electron donor having lower oxidation potential than that of **1**[27] suggests the involvement of the radical cation of the latter.

The curved nature of the quenching plot suggests the involvement of two quenching processes, as has been noted elsewhere[9d]. Radical cation $1^{+\cdot}$ may be formed by donation of an electron to the hole generated in the irradiated semiconductor. Hydrogen shift may then occur in a concerted or stepwise process. The possibility existed that the radical cation $1^{+\cdot}$ underwent deprotonation forming the uncharged radical $2^{\bullet}$. This could be followed by H abstraction e.g. from the solvent. This possibility was excluded. CdS mediated photoreaction of **1b** performed in CD_2Cl_2 afforded **2b** with no significant (ca. 1.4%) incorporation of deuterium. However, the radical $2^{\bullet}$ might instead be reduced by back transfer of an electron from the semiconductor conduction band to give the anion which, in the next step, could be neutralized by protonation[28].

To test this possibility CdS was washed several times with D_2O (99.7 atom % D) and dried under vacuum at room temperature for 12 h. D_2O saturated methylene chloridu (water content 0.12% by weight, K. Fischer determination) was employed as a solvent. Irradiation of the above sample of semiconductor in the presence of **1b** gave **2b**, again with no significant incorporation of deuterium (1.3%), in agreement with the postulate that the reaction be intramolecular. Thus, the interconversion 1 $\rightleftharpoons$ 2 is, *at least in part* (see below) a [1,3] sigmatropic H shift. Ground state [1,3] sigmatropic migrations of hydrogen are unknown to us although a few examples are known which involve the excited state. Only the antarafacial pathway is allowed by the orbital symmetry rules[29] but is geometrically impossible. The observed stereoselectivity of the CdS mediated interconversion is in favour of a concerted process and the stereochemistry of the products is evidence that the H migration proceeds suprafacially, i.e. through the pathway forbidden for thermal [1,3] H rearrangements of closed shell molecules.

However, the rate of the reaction **1b** $\rightarrow$ **2b** induced by irradiation of D_2O pretreated CdS sample was reduced considerably (ca. 20 times). We have observed that the rates of many CdS mediated reactions are altered by water treatment of CdS however pure the commercial sample may be. The possibility that another pathway might be operative when untreated semiconductor was used cannot be, therefore, excluded. The conclusion is, nonetheless, valid for the material produced via the *treated* CdS.

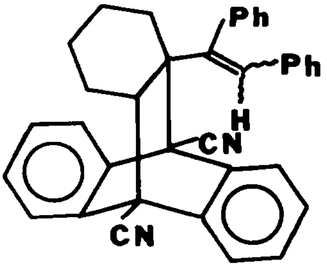
9,10-Dicyanoanthracene sensitized reaction of 1a.

There are several methods to produce radical cation of organic substrates, the generation of which on illuminated semiconductor surface being comparatively recent[3-10,30]. One route, which has been extensively employed, is the electron transfer to an excited, electron deficient sensitizer, e.g. 9,10-dicyanoanthracene (DCA)[31]. The feasibility of photochemical electron transfer in polar solvents can be predicted on the basis of the Weller equation:

$$\Delta G = (E_D^{ox} - E_A^{red}) - E_A^{*} - e_0^2/a\epsilon$$

Calculation of the free energy change, ΔG, using the known values for the reduction potential of the acceptor (E^{red} = -0.89 V vs. SCE[31]), the oxidation potential of the donor (E^{ox} = 1.58 V vs SCE[27]), the excitation energy of the acceptor (E^* = 2.88 eV)[31], and the energy gained by bringing the two radical ions to the encounter distance (a) in a solvent of dielectric constant ϵ, ($e^2/a\epsilon$ ca. 0.06 eV in CH_3CN)[22]; has shown that the electron transfer process from cyclobutene **1a** donor to DCA* acceptor molecule is exothermic by 8 kcal/mol.

Irradiation (λ>400 nm) of a suspension of DCA in CH_3CN containing **1a** led to a rapid consumption of the sensitizer and formation of two isomeric adducts, **7a** (cis) and **7b** (trans), in the ratio 1.8:1 (determined by ^1H NMR spectroscopy.



7a (cis)
7b (trans)

The products were unstable and underwent thermal decomposition as well as oxidative cleavage upon standing on a SiO_2 plate. DCA could be detected amongst the decomposition products in both cases in addition to some other products derived from the second component. Despite thermal instability a low intensity molecular ion was recorded by MS spectroscopy and precise mass determination confirmed the elemental composition (Experimental). Spectral data for 7a and 7b are compatible with the suggested structures. As indicated by molecular models the stilbene chromophore is distorted because of overcrowding. The loss of coplanarity may account for reduction in intensity of the UV absorption band of 7b. The same steric reason could explain the unusual high field location of the vinyl proton[32] which appears in ^1H NMR of 7b as a broad ($\Delta\nu_{1/2}$ = 3Hz) singlet at δ 5.43 ppm. The vinyl proton signal in the cis adduct 7a is additionally shielded (br. singlet, $\Delta\nu_{1/2}$ = 3Hz, δ 4.60 ppm). A molecular model shows that it is now located over the benzene ring of the anthracene moiety.

In agreement with their expected genesis route the formation of the adducts 7 was quenched by 1,2,4-trimethoxybenzene (TMB) to give a linear Stern-Volmer plot (Fig. 2).

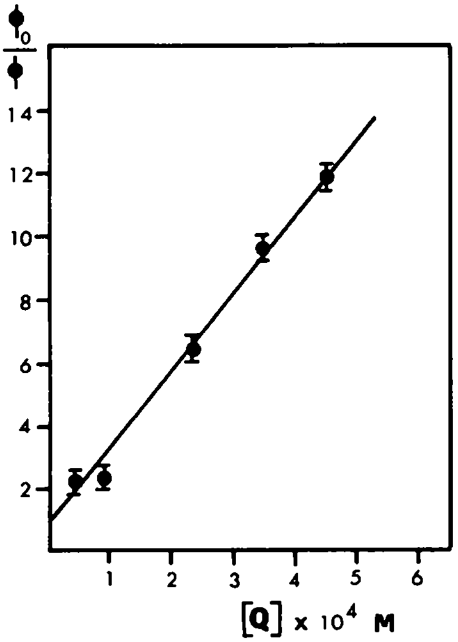


Fig. 2 Quenching of adducts 7 formation by 1,2,4-trimethoxybenzene. [1a] = 2.3 x 10^{-2} M; DCA (15.5 mg) in CH_3CN (5 mL); degassed sample. Slope = 25 x $10^3 M^{-1}$; r = 0.992.

The value of the slope indicates that TMB quenches species other than the excited singlet state of DCA[35]. The formation of the adducts, 7, requires at least two steps, and the detailed mechanism is presently unclear. However, the presence of the $\phi C = C\phi H$ fragment in 7 can be rationalized assuming an initial [1,3] hydrogen shift.

CONCLUSIONS

The interconversion 1 $\rightleftharpoons$ 2, mediated by irradiated suspensions of cadmium sulfide, represents the first example of [1,3] sigmatropic hydrogen shift via a radical cation. No example of such rearrangement proceeding thermally in closed shell molecules is known[29]. Its occurrence through the radical cation is in agreement with theoretical predictions. Calculations for some pericyclic processes have previously shown that ionization should lower the activation energy and therefore facilitate the reaction[11]. A comparison of CdS and DCA photosensitized reactions of 1a is interesting. Although both involve radical cations, as shown by the quenching of the reaction by an appropriate electron donor, the overall outcome of these reactions is different. At least one additional route exists in the homogeneous system: the formation of sensitizer-substrate adducts.

EXPERIMENTAL

Instrumentation.

All the irradiations were performed using a 1 kW PRA Xenon lamp operating as previously described[4]. Corning glass filters 3-72 and 3-73 were used to cut off the irradiation below 420 nm (for the CdS mediated photoreactions) and 400 nm (for the DCA senstized reaction) respectively. Reaction mixtures were analyzed on a Varian 3700 gas chromatograph (GC) equipped with a Hewlett-Packard 3390A integrator. Analyses were made on a 2m x 2mm column packed with OV-101 (10%) on Chromosorb W 80/100. Eicosane was added as internal standard when quantitative GC analyses were performed. DCA sensitized reactions were analyzed by Varian Vista 5500 HPLC with absorbance (Varian UV-200) detector on C_{18}-RP column (Varian Micro-Pak MCH-10). A mixture of acetonitrile-water was used as the solvent system. Adducts **7a** and 7b were not separated under these conditions and their formation and quenching were quantitatively analyzed together. NMR spectra were taken in $CDCl_3$ solution using a Varian XL-200 (^1H NMR) and Varian XL-300 (^{13}C NMR) spectrometer and are calibrated in parts per million (δ) from tetramethylsilane as an internal standard. MS spectra were recorded on Finigen MAT 8230 spectrometer at 70 eV. UV absorption spectra were obtained on Cary 219 spectrophotometer.

Materials.

Spectrograde dichloromethane, acetonitrile (Baker or BDH) and dichloromethane-d_2 (99.8 atom % D, MSD Isotopes) were used as solvents. In all experiments high purity cadmium sulfide (Strem, ultrapure > 99.99%) was used. 9,10-Dicyanoanthracene (Kodak) was crystallized twice from pyridine. 1,2,4-Trimethoxybenzene (97%, Aldrich) was used without further purification 7,8-Diphenylbicyclo[4.2.0]oct-7-ene(**1a**), 8,9-diphenylbicyclo[5.2.0]non-8-ene (**1b**), 7,8-diphenyl-2-oxa-bicyclo[4.2.0]oct-7-ene (1c)[16] and 1,2-diphenyl-cyclobutene[38] were synthesized according to the reported procedures. Merck silica gel: 60-80 mesh (column), GF_{254} (preparative layer) and plates 60 F_{254} (thin layer) were used in separation procedures. Hydrocarbon solvents (cyclohexane, pentane) were used as eluents in the case of **1a-c**; **2a,b**; **3a**; and pentane - CH_2Cl_2 (2:1) mixture to separate oxidation products **5** and **6** obtained from 1d.

General procedure for CdS mediated photoreactions.

All reactions were performed in a Pyrex tube using 5 mL of 3.10-0.36 x 10^{-2}M solutions of cyclobutenes 1, 2 in methylene chloride and 100 mg of CdS. Prior to irradiation the suspensions were sonicated for 10 min. degassed by the freeze-thaw method up to a residual pressure < 2 x 10^{-5} mm Hg, and sealed. In some cases where noted samples were open to the atmosphere via a reflux condenser. The samples were constantly stirred during the irradiation. After the irradiation the semiconductor was filtered off and the sample analyzed by GC. In preparative experiments the collected irradiated samples were separated using SiO_2 plates.

Products 1a, 2a were identified by isolation and a comparison of their ^1H NMR, MS, and UV spectral data with those of authentic samples. The identity of 1b was established by a comparison of its GC retention time, TLC R_f value, and UV spectrum with those of 8,9-diphenylbicyclo[5.2.0]non-8-ene[16]. Spectral data for

2b are presented below. Dibenzoylethane, **5**, and 1-phenylcyclopropyl phenyl ketone, **6**, were isolated and characterized spectroscopically. The data are in full agreement with those reported[23,24]. Identified products and yields are presented in the Table. For all reactions reported appropriate control experiments indicated that both CdS and light were required.

Preparation of cis (2a) and trans (3a) 7,8-diphenylbicyclo[4.2.0]oct-6-enes.

900 mg (3.46 mmol) of **1a** were dissolved in 15 mL of 2.6 M solution of trifluoroacetic acid in benzene. The solution was kept under a nitrogen atmosphere at room temperature for 3.5 h. TLC and GC analyses revealed the presence of three products. The benzene solution was washed with water and dried over $CaCl_2$. Flash chromatography (cyclohexane) gave 592 mg of unreacted starting material and 112 mg (36% yield, based on material reacted) of the mixture of cis and trans isomers (in the ratio cis/trans = 2:1 by ^{1}H NMR). The mixture was separated by preparative thin layer SiO_2 chromatography (pentane, multiple runs), Pure cis, **2a**, and trans, **3a**, isomers were obtained as colorless oils.

2a: UV(cyclohexane) λ_{max} 268 nm (18.600); ^{1}H NMR: 7.28-7.12 (m, 10, aromatic H), 4.41-4.37 (dd, 1, H_8, J = 5.1 Hz and 3.0 Hz), 2.96-2.87 (m, 1, C=C-CH), 2.83-2.74 (m, 1, H_1), 2.50-0.70 (m, 7, CH_2); ^{13}C NMR: 147.8 (C_7), 140.5 (C_6), 135.4 (C_1'), 132.4 (C_1''), 128.5 (C_2' and C_6'), 128.2 (C_3' and C_5'), 127.8 (C_4'), 126.2 (C_2'' and C_6''), 126.1 (C_3'' and C_5''), 125.7 (C_4''), 49.09 (C_8), 43.9 (C_1), 27.7, 27.4, 27.1 and 24.6 (C_2-C_5); MS m/e (rel. int.): $M^{+\cdot}$ +1 261 (22), $M^{+\cdot}$ 260 (100), 245(5), 232 (8), 231 (11), 217 (13), 203 (6), 202 (7), 191 (6), 178 (33), 169 (13). Precise mass: Calcd. for $C_{20}H_{20}$: 260.15650, found: 260.15626.

3a: UV(cyclohexane): λ_{max} 262 nm; ^{1}H NMR: 7.27-7.12 (m, 10, aromatic H), 3.76-3.74 (m, 1, H_8), 2.94-2.85 (m, 1, C=C-CH), 2.40-2.18 (m,3, H_1 and CH_2), 1.92-1.75 (m, 2, CH_2), 1.40-1.32 (m, 3, CH_2); MS m/e (rel. int.): $M^{+\cdot}$ 260 (100), 218 (3), 217 (42), 141 (6), 86 (30). Precise mass: Calcd. for $C_{20}H_{20}$: 260.15650; found: 260.15572.

Thermolysis of 2a

10 mg of **2a** were heated in a sealed tube at 160°C (oil bath) for 3 h and then the ^{1}H NMR spectrum was taken: 7.45 (s, 10, aromatic H); 6.66 (s, 1, ϕCH); 5.58 (m, 1, C=CH), 2.20-1.50 (m, 8, CH_2).

Spectral data for 2b

The product was obtained by CdS photocatalyzed reaction of **1b**. Separation on preparative SiO_2 plates gave **2b** as a colorless oil.

UV(hexanes) λ_{max} 266 nm; ^{1}H NMR: 7.30-7.04 (m, 10, aromatic H), 4.30-4.24 (m, 1, ϕCH), 3.14-2.96 (m, 1, cyclobutyl H), 2.92-2.50 (m, 2, C=C-CH and H_{2a}), 2.08-1.72 (m, 3, CH_2), 1.64-1.00 (m, 4, CH_2), 0.80-0.60 (m, 1, CH_2); MS m/e (rel. int.): $M^{+\cdot}$ + 1 275 (18), $M^{+\cdot}$ 274 (76), 232 (10), 231 (34), 219 (16), 218 (46), 217 (100), 216 (22), 215 (27), 205 (22), 204 (14), 203 (14), 202 (32), 183 (119), 179 (14), 178 (22). Precise mass: Calcd. for $C_{21}H_{22}$: 274.17226, found: 274.17206.

DCA sensitized reaction of 1a

A stirred suspension of DCA (27 mg, 0.12 mmol) in 12 mL of acetonitrile containing **1a** (67 mg, 0.26 mmol) was irradiated in a pyrex tube at λ>400 nm. High purity argon was bubbled through the solution 30 min. before and during the irradiation: the temperature of the sample was kept at 20° ± 1°C. After 2 h of irradiation almost all the DCA was consumed. The solvent was evaporated under reduced pressure, the residue dissolved in 1 mL of acetonitrile and filtered from small amount of unreacted DCA. The filtrate was evaporated to dryness.

Fractional crystallization of the residue (benzene-pentane, 5°C) gave pure cis **7a** (30 mg) and trans **7b** (10 mg) adducts.

7a: UV(CH_3OH): λ_{max} 292 nm (9.200); ^1H NMR: 8.00-6.82 (m, 18, aromatic H), 4.60 (br. s, $\Delta\nu_{1/2}$ = 3 Hz, 1, C=CH), 3.66 (m, 1, -CH), 2.21-1.01 (m, 8, CH_2); MS m/e (rel. int.): $M^{+\cdot}$ 488 (0.1), 461 (0.2), 261 (43), 260 (61), 229 (23), 228 (100), 218 (23), 203 (8), 202 (9), 201 (8), 178 (13), 158 (7). Precise mass: Calcd. for $C_{36}H_{28}N_2$: 488.22525, found: 488.22272.

7b: UV (CH_3OH): λ_{max} 290 nm (13.000); ^1H NMR: 7.85-6.82 (m, 18, aromatic H), 5.43 (br. s, $\Delta\nu_{1/2}$ = 3 Hz, 1, C=CH), 3.68 (m, 1, -CH), 2.14-1.00 (m, 8, CH_2); MS m/e (rel. int.): $M^{+\cdot}$ 488 (0.1), 461 (0.2), 261 (12), 260 (57), 229 (35), 228 (100), 218 (16), 203 (14), 202 (18), 201 (11), 179 (5), 178 (25), 158 (14). Precise mass: Calcd for $C_{36}H_{28}N_2$: 488.22525, found 488.22272.

REFERENCES AND NOTES

1. Publication No. 369 from the Photochemistry Unit, Department of Chemistry, The University of Western Ontario.
2. On leave from A. Mickiewica University, Poznan, Poland.
3. Barber, R.A.; de Mayo, P.; Okada, K. J. Chem. Soc., Chem. Commun. **1982**, 1073-1074.
4. Draper, A.M.; Ilyas, M.; de Mayo, P.; Ramamurthy, V. J. Am. Chem. Soc. **1984**, *106*, 6222-6230.
5. Al-Ekabi, H.; de Mayo, P. Tetrahedron in press.
6. Okada, K.; Hisamitsu, K.; Mukai, T. J. Chem. Soc., Chem. Commun. **1980**, 941-942.
7. Okada, K.; Hisamitsu, K.; Takahashi, Y.; Hanaoka, T.; Miyashi, T.; Mukai, T. Tetrahedron Lett. **1984**, *25*, 5311-5314.
8. Al-Ekabi, H.; de Mayo, P. J. Phys. Chem. in press.
9. (a) Al-Ekabi, H.; de Mayo, P. J. Chem. Soc., Chem. Commun. **1984**, 1231-1232. (b) Hasegawa, T.; de Mayo, P. J. Chem. Soc., Chem. Commun. **1985**, 1534-1535. (c) Al-Ekabi, H.; de Mayo, P. J. Phys. Chem. **1985**, *89*, 5815-5821. (d) Hasegawa, T.; de Mayo, P. Langmuir **1986**, *2*, 362-368.
10. (a) Kodama, S.; Yabuta, M.; Kubokawa, Y. Chem. Lett. **1982**, 1671-1674. (b) Kodama, S.; Yabuta, M.; Anpo, M.; Kubokawa, Y. Bull Chem. Soc. Jpn. **1985**, *58*, 2307-2310. (c) Yanagida, S.; Mizumoto, K.; Pac, C. J. Am. Chem. Soc. **1986**. *108*, 657-654.
11. Bauld, N.L.; Bellville, D.J.; Pabon, R.; Chelsky, R.; Green, G. J. Am. Chem. Soc. **1983**, *105*, 2378-2382 and refs. cited therein.
12. Dass, C.; Gross, M.L. J. Am. Chem. Soc. **1983**, *105*, 5724-5729.
13. The only previously reported sigmatropic reactions were an idiosyncratic zeolite-induced Cope rearrangement[14], and the rearrangement of a methylenecyclopropane derivative[7].
14. Lorenz, K.; Bauld, N.L. J. Catal. 1985, *95*, 613-616.
15. de Mayo, P.; Wenska, G. J. Chem. Soc. Chem. Commun. in press.
16. Kaupp, G.; Stark, M. Chem. Berichte. **1978**, *111*, 3608-3623.
17. $^4J_{HH}$ in strained bicyclic molecules has been observed. In almost all molecules a "W" arrangement of interacting protons was found[18].
18. Barfield, M.; Chakrabarti, B. Chem. Rev. **1969**, *69*, 757-778.
19. Homoallylic coupling ($^5J_{HH}$) may be the cause for broadening of the H_8 signal in 3a.
20. (a) Masamune, S. Tetrahedron Lett. **1965**, 945-951. (b) Pomerantz, M.; Wilke, R.N.; Gruber, G.W.; Roy, U. J. Am. Chem. Soc. **1972**, *94*, 2752-2758.

21. Häussinger, P.; Kresze, G. Tetrahedron **1978**, *34*, 689-696.
22. Eriksen, J.; Foote, C.S. J. Am. Chem. Soc. **1980**, *102*, 6083-6088.
23. Friedrich, L.E.; Fiato, R.A. J. Org. Chem. **1974**, *39*, 416-418.
24. Newman, M.S.; Kaugars, G. J. Org. Chem. **1966**, *31*, 1379-1383.
25. Ripoll, J.L.; Conia, J.M. Bull Soc. Chim. France, **1965**, 2755-2762.
26. Zweig, A.; Hodgson, W.G.; Jura, W.H. J. Am. Chem. Soc. **1984**, *86*, 4124-4129.
27. Presumably the oxidation potential of 1 is close to that of cis-stilbene: 1.58 V vs. SCE [9d].
28. This mechanism has analogy, *interalia* in the sensitized (e transfer) cyanation of phenyl olefins: Maroulis, A.J.; Shigemitsu, Y.; Arnold, D.R. J. Am. Chem. Soc. **1978**, *100*, 535-541.
29. March, J. "Advanced Organic Chemistry", John Wiley & Sons: New York, 1985; pp. 1014-1016.
30. Fox, M.A. Acc. Chem. Res. **1983**, *16*, 314-321.
31. Mattes, S.L.; Farid, S. in "Organic Photochemistry", Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p.234.
32. Loss of coplanarity because of the presence of a bulky group in substituted trans-stilbenes causes a reduction in intensity of the long wavelength UV absorption band [33]. The broadening of $HC\phi{=}C\phi$ signal and its upfield shift in ^{1}H NMR spectra of substituted stilbenes have also been reported[34].
33. Bromberg, A.; Muszkat, K.A. Tetrahedron **1972**, *28*, 1265-1274.
34. Casy, A.F.; Parulkar, A.; Pocha, P. Tetrahedron **1968**, *24*, 3031-3041.
35. The limiting value of the slope for ^{1}DCA* quenching, would be, assuming that the process is diffusion controlled: $k_q\tau = 196\ M^{-1}$ (k_q ca. $10^{10}\ M^{-1}$, ^{1}DCA* lifetime $\tau = 19.6$ ns in CH_3CN[36]) but, in fact, is $2.5 \times 10^3\ M^{-1}$. On the other hand, the trans-stilbene radical cation lifetime has been reported to be in the microsecond range[37].
36. Mattes, S.L. Farid, S. J. Am. Chem. Soc. 1983, *105*, 1386-1387.
37. Hub, W.; Klüter, U.; Schneider, S.; Dörr, F.; Oxman, J.D.; Lewis, F.D. J. Phys. Chem. **1984**, *88*, 2308-2315.
38. Newman, M.S.; Kaugars, S. J. Org. Chem. 1965, *30*, 3295-3298.