111. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.03; H, 9.40.

5-Phenylpenta-2,4-dienoic Acid Methyl Ester, 5-Phenylpenta-2,4-dien-1-ol, and 5-Phenylpenta-2,4-dienyl 1-Acetate (3). These are synthesized as per the above sequence. 5-Phenylpenta-2,4-dienoic acid methyl ester (95% yield): mp 78 °C; ^{1}H-NMR 6.0 (d, 2 H, J = 15.8 Hz), 7.2–7.5 (3 H and aromatic), 6.9 (m, 4 H and 5 H), 3.8 (s, $COOCH_3$); ^{13}C-NMR 14.19, 60.15, 121.19, 126.09, 127.04, 127.81, 128.64, 128.96, 135.88, 140.19, 144.38, 166.85; mass fragments 202 (M^+), 173, 157, 129. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.2; H, 6.98. Found: C, 77.15; H, 6.95. 5-Phenylpenta-2,4-dien-1-ol (60% yield): mp 67 °C; ^{1}H-NMR 5.92 (m, 2 H, J_{2H-3H} = 15.8 Hz), 6.78 (dxd, 3 H), 6.4 (q, 4 H, J_{4H-3H} = 16.0 Hz), 6.55 (d, 5 H, J = 16 Hz), 7.2–7.5 (m, aromatic), 4.25 (d, CH_2OH); ^{13}C-NMR 63.33, 126.34, 127.58, 128.11, 128.57, 129.03, 131.55, 132.46, 132.71, 137.06; mass fragments 160 (M^+), 142, 129. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.56; H, 7.57. 5-Phenylpenta-2,4-dienyl 1-acetate (3): ^{13}C-NMR 20.87, 64.66, 126.4, 126.79, 127.61, 128.54, 133.68, 134.44, 136.82, 170.67; mass fragments 202 (M^+), 159, 129. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.05; H, 7.04.

Methyl ethers were prepared by extending the published procedure to the present systems.[20]

β-Ionylideneethanol methyl ether (4): 80% yield; mass fragments 234 (M^+), 219, 212, 189. Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.89; H, 11.39.

3,7-Dimethylocta-2,4,6-trienyl methyl ether (9): 75% yield; mass fragments 166 (M^+), 151, 134, 121. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.36; H, 11.03.

5-Phenylpenta-2,4-dienyl methyl ether (10): 80% yield; ^{13}C-NMR 57.93, 72.78, 126.38, 126.80, 127.59, 128.22, 128.59, 129.94, 132.73, 132.93; mass fragments 174 (M^+), 159, 142, 128, 115. Anal. Calcd for $C_{12}H_{14}O$: C, 82.62; H, 8.10. Found: C, 82.62; H, 8.20.

Retinyl methyl ether (11): 70% yield; mass fragments 300 (M^+), 285, 268, 255. Anal. Calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73. Found: C, 83.12, H, 10.80.

Anhydroretinol (12) was prepared as per the reported procedure:[21] mass fragments 268 (M^+), 253, 205, 107. Anal. Calcd for $C_{20}H_{28}$: C, 89.49; H, 10.51. Found: C, 89.13; H, 10.68.

Photolysis. A rayonet photochemical reactor equipped with RPR-2537 (254 nm) lamps was used for the irradiation of compounds 1–4; a 450-W medium-pressure Hg arc lamp was used for the irradiation of 5. All reactions were monitored by Shimadzu LC-6A with a UV–visible detector and coupled with a CR-3A integrator. An amino silica column, 4.6/250 mm, was used with hexane as eluent for all the systems. In sensitization experiments, the sensitizers were well-separated on LC conditions and did not interfere with polyenes, except in the case of 3. Variation in light intensity was achieved by reducing the number of lamps used in the Rayonet photochemical reactor. A typical experiment involved 10 mL of a 10^{-3} M solution of 1–4. The polyene solution was purged with nitrogen gas in a quartz tube and irradiated with 254-nm lamps in a Rayonet reactor. After the irradiation, products were characterized based on the spectral information and comparison with the authentic samples. Prolonged irradiation leads to other products.

Fluorescence spectra were obtained on a SPEX-Fluorolog fluorimeter. Analytical-grade solvents were used. Identical conditions were maintained for all the fluorescence measurements. A xenon arc lamp equipped with the fluorescence instrument was used for the excitation. The excitation wavelength was 320 nm, the slit width was 4 mm, and the emission spectral range was 330–600 nm; all operations were at room temperature. 9,10-Diphenylanthracene was the standard (ϕ_f = 1.0). Relative quantum yield of fluorescence was calculated as per Calverts and Pitts.[7] A 2×10^{-4} M concentration of 5 was used for fluorescence measurements in all solvents.

Quantum yields were determined in an Applied Photophysics Model QYR-20 quantum yield reactor equipped with a 200-W Hg arc lamp. Solution filters were used to isolate the required wavelength band. Quantum yield of product formation for 5 was determined in various solvents. The quantum yields of product formation for 1–4 were determined in methanol. Potassium ferrioxalate was used as an actinometer.

Acknowledgment. We thank Prof. R. S. H. Liu, University of Hawaii, Honolulu, for the kind suggestions. We thank Dr. A. V. Rama Rao, Director, IICT, and Dr. U. T. Bhalerao, Deputy Director, IICT, Hyderabad, India, for their encouraging support in these investigations. IICT Communication No.: 2877.

---

(20) Ando, T.; Yamawaki, J.; Kawate, T.; Sumi, S.; Hanafusa, T. *Bull. Chem. Soc. Jpn.* 1982, *55*, 2504.

(21) Sahntz, E. M.; Cawley, J. D.; Embree, N. D. *J. Am. Chem. Soc.* 1943, *65*, 901.

Double Group-Transfer Reactions: A Theoretical (AM1) Approach

Antonio Frontera, Guillem A. Suñer, and Pere M. Deyà*

Departament de Quimica, Universitat de les Illes Balears, 07071-Palma de Mallorca, Spain

Received April 7, 1992

The mechanisms of several concerted and stepwise dyotropic transfer reactions have been studied using the AM1 semiempirical SCF-MO procedure. Dihydrogen transfer on cyclobutene is best described by means of a stepwise diradical pathway. Moreover, the symmetric stationary point corresponding to the concerted reaction is no longer a true transition state. In contrast, the thermal intramolecular isomerization of diaxial 2,3-dibromo-*tert*-butylcyclohexane to the diequatorial isomer is a concerted process with an energy barrier of 62.2 kcal mol^{-1}. The activation energy of the concerted dyotropic transfer in *syn*-sesquinorbornene systems (i.e., pentacyclo[7.6.0.$0^{2,13}$.$0^{3,8}$.$0^{10,14}$]pentadeca-4,6,11-triene) is linearly dependent of the size of the intracavity gap ($C–H \cdots C_{sp2}$), thus in agreement with Menger's spatiotemporal hypothesis.

The concerted transfer of two hydrogen atoms from an eclipsed ethane to an ethylene group is a thermally allowed pericyclic [$\sigma^2s + \sigma^2s + \pi^2s$] reaction.[1] Other well-known examples involving the transfer of two hydrogen atoms on different substrates such as the reduction of alkenes with diimide species,[2] and related reactions with hydrocarbons,[3] have also been mechanistically interpreted as involving such types of processes.

---

(1) Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1971; pp 141–144.

(2) See, for example: Van Tamelen, E. E.; Dewey, R. S.; Lease, M. F.; Pirkle, W. H. *J. Am. Chem. Soc.* 1961, *83*, 4302. Hünig, S.; Müller, H. R.; Thier, W. *Angew. Chem., Int. Ed. Engl.* 1965, *4*, 271. Garbisch, E. W., Jr.; Schildcrout, S. M.; Patterson, D. B.; Sprecher, C. M. *J. Am. Chem. Soc.* 1965, *87*, 2932. Willis, C.; Back, R. A.; Parsons, J. M.; Purdon, J. G. *J. Am. Chem. Soc.* 1977, *99*, 4451. Franck-Neumann, M.; Dietrich-Buchecker, C. *Tetrahedron Lett.* 1980, 671.

The analogous intramolecular rearrangement is generally referred to as a dyotropic reaction.[4] The thermoneutral transfer of hydrogen on oxatetracyclododecenes,[5] sesquinorbornene disulfones,[6] or on several heterocyclic bridged-ring systems[7] are well-known examples of dyotropic reactions. The migrating groups in these processes are not restricted to hydrogen atoms only. Thus, the intramolecular isomerization of 5,6-dibromocholestane,[8] in which two C–Br σ-bonds interchange their positions (with inversion of configuration of both C-5 and C-6) has also been considered a dyotropic process.[9]

In this paper we describe that the AM1[10] semiempirical method is a valuable tool for carrying out theoretical studies of the above mentioned double group-transfer reactions. We have tested this methodology on a number of reactions previously described in the literature and have found good agreement with experimental data.

First, we chose for study a hypothetical prototype reaction belonging to the cyclobutene system. The aim of this preliminary calculation was to examine the alternative pathways corresponding to the concerted and the stepwise mechanisms and locate the different transition structures and/or intermediates. On the other hand, we expected this reaction to be an adequate model for other 2H group-transfer reactions in alicyclic and heterocyclic bridged-ring systems.[3]

We have also extended our study to known (experimentally observed) reactions for which kinetic data are available. We present herein the results on the thermal mutarotation of 2,3-dibromo-*tert*-butylcyclohexane and the dyotropic hydrogen migration in pentacyclo[7.6.0.0^{2,13}.0^{3,8}.0^{10,14}]pentadeca-4,6,11-triene. The most important conclusion that can be drawn from this study is that AM1 closely reproduces the experimental data described in the literature.

Theoretical Methods

Molecular orbital calculations on reactants, intermediates, transition structures and reaction products were performed by using the semiempirical AM1[10] method implemented in a modified version[11] of the MOPAC program.[12] RHF functions were used for closed-shell systems. For biradical systems the open-shell "half-electron" approximation with 3 × 3 CI (AM1-HE-CI) was used.[13]

The construction of the potential energy surfaces was carried out by means of two reaction coordinate methods, i.e., (a) by using the standard methodology, where the variation of a simple geometrical parameter (bond length, bond angle, or dihedral angle) is used as the reaction coordinate, with symmetry constrains, if required; and (b) by defining the reaction coordinate (R) as a function of several geometrical parameters; in our case, minimum energy reaction pathways (MERP) were calculated by means of eq 1.

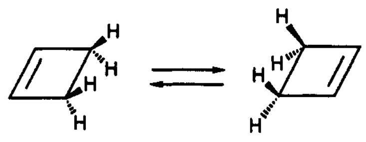


Figure 1.

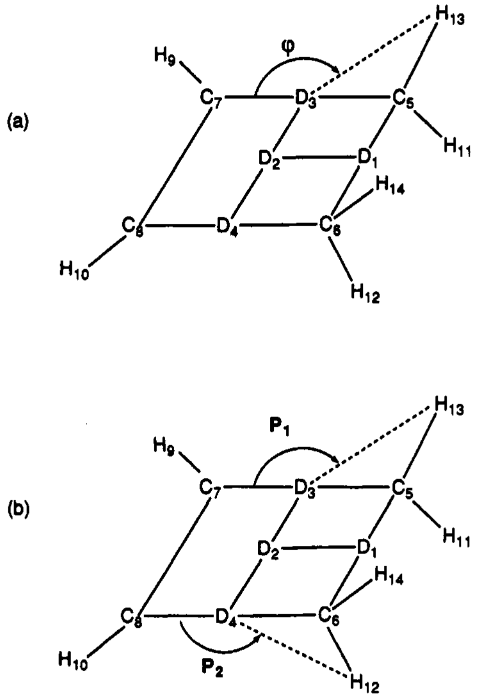


Figure 2. Reaction coordinate systems used for the construction of the potential energy surfaces for the dyotropic reaction on cyclobutene. D represents a mathematical point (dummy atom) used to facilitate the geometry definition: (a) standard reaction coordinate method; (b) parameters of eq 1.

$$R = P1 + P2 + Z \tag{1}$$

Here, the reaction coordinate (R) is equal to the sum of the lengths of the two breaking (or forming) bonds (alternatively, the sum of two angles or dihedral angles may be used) and Z is a constant needed to avoid undesirable values for R (i.e., negative or larger than 180°) when angles are used instead of bond distances. Actually when $P1$ and $P2$ are bond distances, Z should be zero (see below for a more detailed explanation about how eq 1 works).[14] In this manner, the energy was minimized with respect to all other geometrical variables without imposing any further restriction. In all cases a potential energy curve showing a continuous variation of energy was obtained. It should be remarked that the reaction coordinate so defined does not require that the two parameters ($P1$ and $P2$) are identical along the reaction path, thereby allowing for the study of concerted and nonconcerted pathways in a very simple manner.

All stationary points were located on the potential energy surfaces, and the corresponding geometries were subsequently refined by minimizing the energy (for minimums) or the norm of the gradient[15] (for saddle points) with full optimization of all geometric variables (bond lengths, bond angles, and dihedral angles) without further symmetry restrictions.[16] Stationary points on the potential energy surfaces were characterized according to the number of negative vibrational frequencies.[15]

---

[3] Mackenzie, K. *J. Chem. Soc.* **1965**, 4646. Mackenzie, K. *J. Chem. Soc. C* **1969**, 1784.

[4] Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 129, 131. Reetz, M. T. *Tetrahedron* **1973**, *29*, 2189.

[5] Hagenbuch, J.-P.; Stampfli, B.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 3934.

[6] Paquette, L. A.; Kesselmayer, M. A.; Rogers, R. D. *J. Am. Chem. Soc.* **1990**, *112*, 284.

[7] Mackenzie, K.; Proctor, G.; Woodnut, D. J. *Tetrahedron* **1987**, *43*, 5981.

[8] Mauthner, J. *Monatsh. Chem.* **1906**, *27*, 421.

[9] Barton, D. H. R.; Head, A. J. *J. Chem. Soc.* **1956**, 932.

[10] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[11] Olivella, S. *QCPE Bull.* **1984**, *4*, 10. Extended by S. Olivella and J. M. Bofill.

[12] VAX version: Stewart, J. J. P. *QCPE Bull.* **1983**, *3*, 101.

[13] (a) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92. Salem, L. *Pure Appl. Chem.* **1973**, *33*, 317. (b) Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771.

[14] Equation 1 is a modification of a reaction coordinate previously described. See: Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9095.

[15] McIver, J. W.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[16] All calculations have been carried out with the keywords PRECISE and GNORM = 0.01.

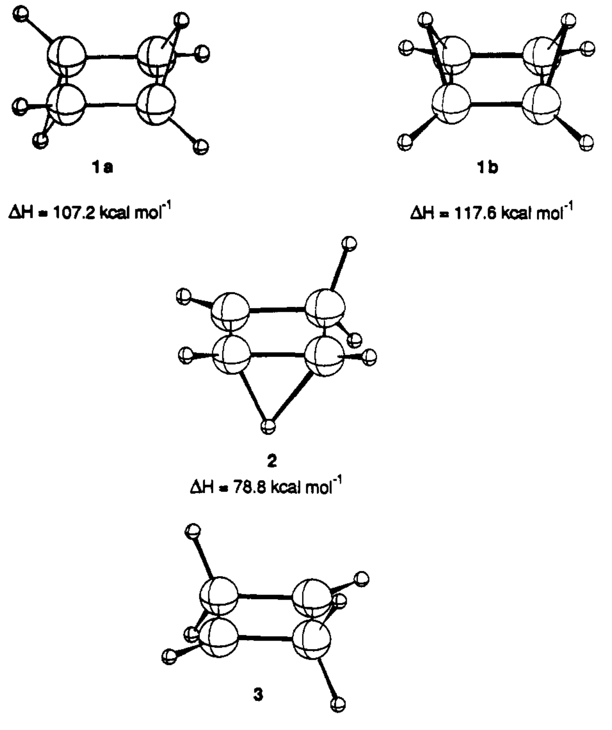


Figure 3. Relative energies of stationary points on the potential surface for dyotropic reaction on cyclobutene (all energies are relative to cyclobutene). Energy values for 2 and 3 have been corrected by adding 14 kcal mol^{-1} to the 3×3 CI energy as suggested in ref 20b.

Thermodynamic properties (entropies and specific heats) were obtained from the calculated geometries and vibrational frequencies as previously described.[17]

Results and Discussion

Our initial calculations were carried out on the hypothetical unrealistic[18] dyotropic reaction shown in Figure 1.

The first step in our investigation was to determine the geometrical and electronic requirements of the transition states for (a) the two possible concerted processes ((*i*) $[\sigma^2s + \sigma^2s + \pi^2s]$: both hydrogen atoms migrate through the same side of the molecular plane, and (ii) $[\sigma^2s + \sigma^2a + \pi^2a]$: one hydrogen atom migrates on each side of the plane)[19] and (b) nonconcerted rearrangements for which energy and geometric parameter of the corresponding intermediates were also needed. For this purpose, we carried out a detailed analysis of the different possible pathways for this process.

The symmetrical synchronous pathways were calculated at the RHF Hartree–Fock level using the standard reaction coordinate method. The variation of the angle φ defined by atoms C7–D3–H13 in Figure 2a was the reaction coordinate and the following symmetry restrictions were imposed: angles C7–D3–H13 and C8–D4–H12 (or C8–D4–H14) in Figure 2a are identical. By so doing, two stationary points **1a** and **1b** (Figure 3) were located. The corresponding energy barriers are 107.2 and 117.6 kcal/mol, respectively. It is worth remarking that the synchronous stationary points **1a** and **1b** (Figure 3) are not true transition states since they have two negative roots in the force constant matrix.

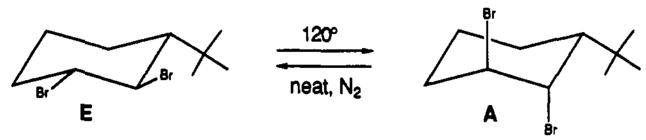


Figure 4. Intramolecular isomerization of 2,3-dibromo-*tert*-butylcyclohexane.

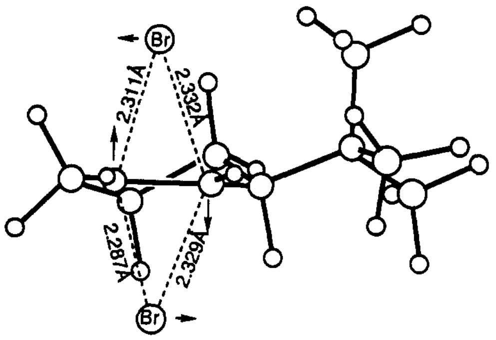


Figure 5. Normal mode corresponding to a displacement along the reaction coordinate at the transition state of the dyotropic transfer of the two Br atoms (see Figure 4).

On the other hand, we have also carried out calculations using the reaction coordinate defined in eq 1, *P*1 and *P*2 being the angles shown in Figure 2b. Two new stationary points were located (**2** and **3** in Figure 3) which correspond to a genuine transition state and a biradical intermediate, respectively. The energy barrier for this stepwise process (78.8 kcal/mol) is considerably lower than the corresponding synchronous concerted alternative pathways.[20] Due to the biradical character of **2** and **3**, a HE-CI open-shell treatment was employed, as mentioned previously.

Thus, at the AM1 level of theory, the stepwise stationary point **2** is actually the only genuine transition state between cyclobutene and the intermediate biradical **3**. In other words, by using the reaction coordinate method defined in equation 1 with no further symmetry constrains, we found that the MERP for this reaction corresponds to the nonconcerted mechanism.

***trans*-2,3-Dibromo-*tert*-butylcyclohexane.** The addition of bromine (chloroform, 0 °C) to *tert*-butylcyclohexene yields a mixture of *trans*-2,3-dibromides **E** (diequatorial) and **A** (diaxial) in a 3:4 ratio. Berti et al.[21] reported that the two dibromides thermally equilibrate (Figure 4), thereby providing a mixture highly enriched in **A**.

As shown below, this equilibration might occur via a dyotropic process. Furthermore, our calculations are in agreement with this preference for the diaxial **A** over the diequatorial dibromide **E** (ΔG_{393} = −0.85 kcal/mol).[22]

AM1-RHF closed-shell calculations carried out by means of the reaction coordinate method described above (eq 1: *P*1 and *P*2 are the Br–C–C angles) show a continuous

---

[17] Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* 1977, *99*, 7822.

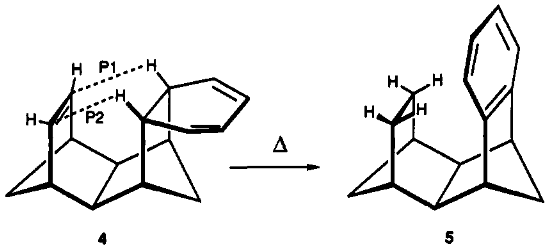
[18] The competing electrocyclic ring opening to butadiene and subsequent ring closure is obviously lower in energy. See: Criegee, R.; Seebach, D.; Winter, R. E.; Börretzen, B.; Brune, H. A. *Chem. Ber.* 1965, *98*, 2339.

[19] Both processes are thermally allowed by the Woodward–Hoffmann rules (see ref 1).

[20] (a) Note that this value is higher than the corresponding AM1 calculated value for the electrocyclic ring opening (ΔH = 36.0 kcal/mol). See ref 10. (b) Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *J. Am. Chem. Soc.* 1978, *100*, 5650.

[21] Barili, P. L.; Belluci, G.; Berti, G.; Marioni, F.; Marsili, A.; Morelli, I. *Chem. Commun.* 1970, 1473.

[22] Berti et al.[21] report that ΔG_{393} is larger than 3.6 kcal/mol according to which E should be more stable than A. By comparing the dipole–dipole interactions in the calculated A and E structures and the corresponding 2,3-cyclohexanes we have not found any significant destabilization due to such interaction, as hypothesized by Berti. Our value is more in accordance with those determined by Pasto and Rao for substituted 2-*tert*-butylcyclohexanes. See: Pasto, J. S.; Rao, R. D. *J. Am. Chem. Soc.* 1969, *91*, 2790.



4 5

Figure 6.

variation of the potential energy corresponding to the concerted mechanism,[23] the calculated activation free energy (ΔG^{*}_{393}) being equal to 62.2 kcal/mol. The transition structure (Figure 5) is in agreement with that suggested by Barton et al.[9] for the closely related mutarotation of some steroidal 5α,6β-dibromides in nonionizing solvents (see below).

In Figure 5, the arrows show the transition vector[16] for the thermal equilibration of dibromides **E** ⇄ **A**. As shown, the most important shifts correspond to the bromine atoms and the corresponding carbon atoms moving in opposite directions, thus describing the concerted rearrangement.

The above process is apparently related to the long-known mutarotation of dibromocholestane[8] for which Grob and Winstein[24] have suggested an intramolecular mechanism. In particular, for the isomerization of 5α,6β-dibromocholestane to the 5β,6α-isomer, in a number of solvents, these authors suggested the existence of an intermediate (bromonium–bromide ion pair) that changes gradually as the ionizing power of the solvent decreases. For the poorest ionizing solvents an intermediate or transition state with negligible charge separation has been proposed in which both bromine atoms are essentially equivalent. In agreement with these suggestions, Barton[9] hypothesized that, in non-ionizing solvents (close to computational gas-phase conditions), the two-step mechanism merges with a fully concerted process.

2H Group-Transfer Reactions in *syn*-Sesquinorbornene Systems. The stereospecific group-transfer of two hydrogen atoms in a noncatalyzed thermal rearrangement is a typical example of 2H group transfer reaction that has attracted attention both theoretically[25] and experimentally.[3,7,26]

H. S. Rzepa[25b] has reported the results of a systematic investigation of such reactions for a wide variety of hydrogen donors and acceptors using the MNDO and AM1 SCF-MO procedures. According to this study the AM1 method tends to favor concerted and essentially synchronous transfer of hydrogen whereas MNDO tends to favor stepwise mechanisms, the AM1 barriers being in close agreement with previous ab initio results.[27] The author concludes that dihydrogen transfer reactions may provide one means of calibrating semiempirical against ab initio calculations of pericyclic mechanisms.

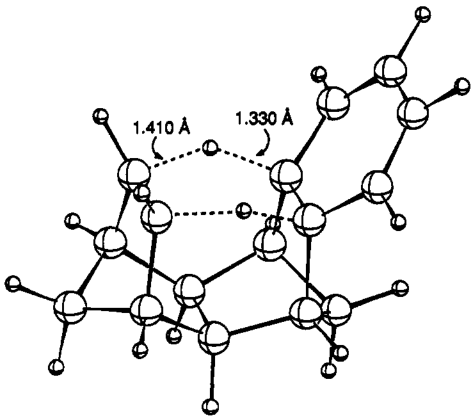
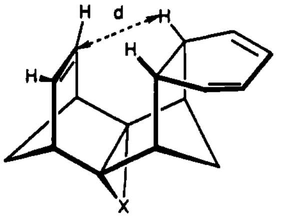


Figure 7. Transition structure for the dyotropic reaction on *syn*-sesquinorbornene 4.



compd	X	d (Å)
4	H,H	2.23
4a	O	2.33
4b	CH_2	2.19
4c	NH	2.20
4d	S	2.23
4e	$-CH_2-CH_2-$	2.18
4f	N-Ph	2.18

Figure 8. Size of the intracavity gap (*d*, in Å) in *syn*-sesquinorbornenes.

Table I. Relative Activation Energies for Dyotropic Hydrogen Migration on *syn*-Sesquinorbornenes (T = 403 K)

compd	d^a (Å)	ΔH^{*b}	ΔS^{*c}	ΔG^{*d}
4	2.23	36.2	–5.5	38.4
4a	2.33	42.5	–4.9	44.5
4b	2.19	35.4	–4.8	37.4
4c	2.20	36.4	–4.8	38.3
4d	2.23	37.4	–5.1	39.4
4e	2.18	34.7	–4.3	36.5
4f	2.18	34.4	–4.7	36.3

[a] Intracavity gap (see Figure 8). [b] Relative heats of activation. In kcal/mol. [c] Relative entropies of activation. In cal/mol K. [d] Relative Gibbs free energies. In kcal/mol.

We have performed AM1 calculations on the reported intramolecular thermoneutral $[\sigma^2s + \sigma^2s + \pi^2s]$ dyotropic transfer of hydrogen in *syn*-sesquinorbornenes[3,7,28] by using eq 1 as the reaction coordinate. In this case $P1$ and $P2$ are the two $H–C_{sp2}$ distances corresponding to the forming bonds (see Figure 6). It is worth mention in this context that, by just controlling the two bond-forming processes, we actually control the two forming and two breaking bonds directly involved in the transfer process because of the rigidity of the *syn*-sesquinorbornene skeleton.

The activation enthalpy found for the dyotropic rearrangement **4** → **5** (Figure 6) is very similar in magnitude (36.2 kcal/mol) to that experimentally determined for the same process on analogous substrates (35–39 kcal/mol).[5] Furthermore, the calculated ΔS^{*} (–5.5 eu) agrees well with the reported values for analogous processes.[29]

The geometry of the transition structure found (Figure 7) suggests that the translocation of the two C–H σ bonds, though not fully symmetrical, can be defined as synchronous, according to Dewar's terminology.[13b]

---

[23] In fact, all attempts to calculate the barrier for the stepwise mechanism by using either UHF or 3×3 CI levels were unsuccessful, as only the concerted path was found. In our opinion a stepwise mechanism through a bromonium–bromide ion pair without solvent participation is hard to accept.

[24] Grob, C. A.; Winstein, S. *Helv. Chim. Acta* **1952**, *35*, 782.

[25] (a) Feller, D. F.; Schmidt, M. W.; Ruedenberg, K. *J. Am. Chem. Soc.* **1982**, *104*, 960. (b) Agrafiotis, D. A.; Rzepa, H. S. *J. Chem. Soc., Chem. Commun.* **1987**, 902. Agrafiotis, D. A.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **1989**, 475.

[26] Feller, D.; Borden, W. T.; Davidson, E. R. *J. Comput. Chem.* **1980**, *1*, 158. Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1981**, *103*, 2558.

[27] For example, the calculated AM1 barrier for the reduction of ethene by cis diimide, 32.3 kcal/mol (see ref 21b), compares reasonably well with the calculated ab initio (4-31G//STO-3G) barrier of 26.7 kcal/mol. See: Pasto, D. J.; Chipman, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 2290.

[28] Chow, T. J.; Ding, M.-F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1121.

[29] The ΔS^{*} values found for type-II dyotropic reactions range from modestly negative (see ref 3) to slightly positive (see ref 5).

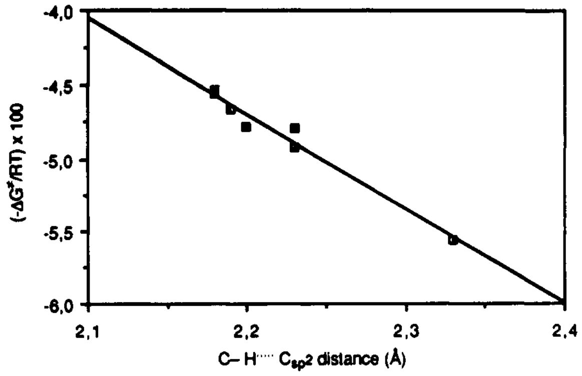


Figure 9. Plot of $-\Delta G^{*}/RT$ versus the C–H···$C_{sp}2$ distance.

In recent papers on dyotropic hydrogen migration on *syn*-sesquinorbornene disulfones, Paquette and co-workers[6,30] concluded that the intracavity gap between the origin of migration and the migration terminus (d, in Figure 8) is an important, although not the exclusive, determinant of rate in these systems. These workers measured rate constants for migration in several such substrates having different sizes of the intracavity gap, thereby proving that the relative *k*'s of the corresponding 2H group-migration are linearly dependent upon the mentioned distance, thus supporting Menger's spatiotemporal hypothesis.[31]

We have carried out an AM1 study of several substrates with different intracavity distances[32] (see Figure 8). The results illustrated in Table I show that the plot of the ΔG^{*} values versus the C–H···$C_{sp}2$ distance (Figure 9) correlates well (correlation coefficient, $r = 0.99$), thus supporting Paquette's explanation.[6,30]

The present results are in good agreement (both qualitative and quantitative) with the experimental data, thus supporting the usefulness of AM1 in evaluating the geometric and electronic effects which control these double group-transfer reactions. This is mentioned since such rearrangements are impossible to tackle by ab initio methods due to the cost in computer time.

Conclusions

The following conclusions can be drawn from the AM1 calculations reported above: (1) Using the reaction coordinate defined by eq 1 allows AM1 calculations of concerted and nonconcerted reactions to be carried out in a simple manner. In our view this reaction coordinate will facilitate the study of other processes involving significant changes of several variables at once.

(2) Our AM1 semiempirical calculations are both in qualitative and quantitative agreement with theoretical and experimental results reported in the literature. The energetics and geometric effects in double group-transfer reactions are accurately reproduced. In our opinion this would be a very useful tool for the organic chemists to explore such processes for predicting purposes.

Acknowledgment. Time allocation for calculations, performed with VAX 8820 and VAX 9000 computers, was generously provided by the Centre de Càlcul de la Universitat de les Illes Balears. We are indebted to Professor José M. Saá (Universitat de les Illes Balears, Spain) for carefully reading the manuscript and making several suggestions for improvement and Professor Santiago Olivella (Universitat de Barcelona, Spain) for helpful discussions and also for making his modified version of MOPAC available to us. Two of us (A.F. and G.A.S.) thank the DGICYT and the Fundació Joan Muntaner for fellowships. Financial support by the DGICYT (Grant PB90-0040) is gratefully acknowledged.

Registry No. 4, 144242-22-8; A, 35190-03-5; E, 38749-33-6; cyclobutene, 822-35-5.

Supplementary Material Available: Listing of Cartesian coordinates of the optimized molecular structures calculated at the AM1 level (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered form the ACS; see any current masthead page for ordering information.

---

(30) Paquette, L. A.; O'Doherty, G. A.; Rogers, R. D. *J. Am. Chem. Soc.* **1991**, *113*, 7761.

(31) Menger, F. M.; Venkataram, U. V. *J. Am. Chem. Soc.* **1985**, *107*, 4706. Menger, F. M. *Acc. Chem. Res.* **1985**, *18*, 128. Sherrod, M. J.; Menger, F. M. *J. Am. Chem. Soc.* **1989**, *111*, 2611.

(32) Five substrates (**4**, **4a**, **4b**, **4c**, and **4f**) are described in Paquette's report.[6] The other two (**4d** and **4e**), as far as we are aware of, have not been described yet, and they have been enclosed here for predicting purposes.