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MNDO Study of the Claisen Rearrangement[1]

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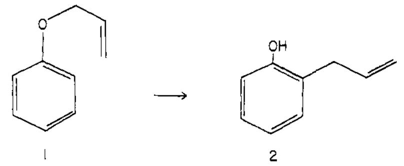
Abstract: MNDO calculations are reported for the Claisen rearrangements of 3-oxa-1-hexene, for its various methoxy and cyano derivatives, and for the 2-methoxy-5-cyano derivative. The reactions are found to take place by a two-stage mechanism, analogous to that of the Cope rearrangement of 2,5-hexadiene but where the intermediate biradicaloid is not a stable species, undergoing conversion to the product without activation. The results agree with the available evidence concerning substituent effects and lead to verifiable predictions.

The term "Claisen rearrangement" was originally applied to rearrangements of allyl aryl ethers to ortho, or occasionally para, phenols, e.g., **1** → **2**. In recent years, however, it has been extended to include the analogous rearrangements of allyl vinyl ethers to unsaturated aldehydes and ketones, e.g., **3** → **4**.[2] The latter reactions are analogues of Cope rearrangements of 1,5-hexadienes (e.g., **5** → **6**) in which one of the saturated carbon atoms is replaced by oxygen and are now likewise classed as [3,3] sigmatropic rearrangements.[3] Until recently it was generally assumed that reactions of this kind take place in a synchronous[4] manner, via aromatic[5,6] transition states (TS), formed by a combination of σ-type and π-type overlap of the 2p AOs of the carbon atoms in the two allyl moieties. As Doering and Roth[7] pointed out some time ago, such a TS can in principle exist in geometries (**7**, **8**) analogous to those of the chair and boat conformers of cyclohexane. They were able to show by an ingenious experiment that the chair TS (**7**) is favored. Similar considerations apply to the Claisen rearrangements of allyl vinyl ethers, and Schmidt et al.,[8] have likewise shown that these too take place via chair-type intermediates, **9**. This evidence shows clearly that neither reaction takes place by fission into radicals and recombination. In each case formation of the new CC bond must begin before the breaking CC (or CO) bond has completely broken.



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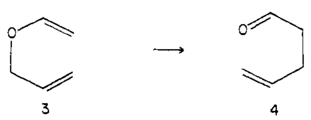

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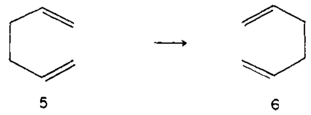
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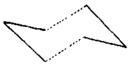
Studies[9] of the effects of phenyl substituents on the rate of rearrangement of 1,5-hexadiene (**5**), and MINDO/3 calculations,[10] have, however, indicated very strongly that the reaction is not only not synchronous[4] but not even concerted,[4] taking place via a biradical-like (*biradicaloid*) species (**10**) as a stable intermediate, a possibility which had indeed been suggested earlier by Doering et al.[11] This mechanism was further supported by the good agreement between the calculated and observed heat and entropy of activation for the rearrangement of **5** and by similar agreement for the difference in rate between rearrangements via chair and boat biradicaloids as intermediates.[9]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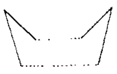
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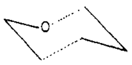

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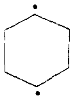
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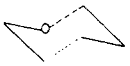

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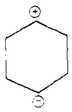

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Studies of isotope effects on the rates of the Cope[12,13] and Claisen[14] rearrangements show that the new CC bond is partly formed in the transition state (TS), as it must be in any intramolecular mechanism. The values of the corresponding rate ratios have also been claimed to show that the reactions are synchronous, but the arguments used are open to criticism.[15] They depend on unfounded assumptions concerning the relationship between secondary isotope effects due to deuteriation and the extent to which an adjacent CC bond has formed or weakened (see ref 16).

The mechanism of the Claisen rearrangement thus presents some very interesting problems, which moreover are very difficult to solve by experiment[16] because they involve the detailed timing of bond making and bond breaking during a reaction. Since no adequate calculations for reactions of this kind have as yet been

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[1] Part 68 of the series Ground States of Molecules. For Part 69, see: Dewar, M. J. S.; Healy, E. F.; Stewart, J. J. P. *J. Comput. Chem.*, in press.

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Table I. Heat of Formation and Entropies

	ΔH_f, kcal/mol		S, cal/mol/K
	calcd	exptl[a]	(calcd at 273 K)
3	−7.24	−8.7	82.54
4	−27.90	−25.8	83.26
16	−46.15		93.30
17	−50.81		93.56
18	24.42		91.16
19	25.72		90.76
20	−19.38		98.41
21	20.12		91.05
22	31.39		92.38
23	22.41		92.25

[a] Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions"; U.S. Department of Commerce: Washington, DC, 1970; NSRDS-NBS-21, p 363.

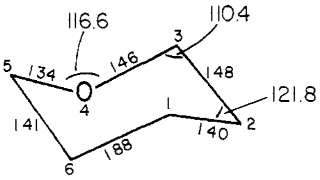

Figure 1. Geometry (bond lengths in Å) calculated for **11**.

reported and since such reactions are also of major importance in synthesis, we decided to study the simplest example, i.e., the rearrangement of allyl vinyl ether (**3**) to 5-hexenal (**4**), using MNDO. We chose this in preference to MINDO/3 because it usually gives better results for heteroatoms. While **3** itself contains only one heteroatom, we also wanted, for reasons indicated below, to study the effects of substituents in the 2- and 5-positions on the rate of rearrangement.

Procedure

The calculations were carried out by using the standard closed shell version of MNDO.[17] Geometries for ground states were determined by minimizing the energy with respect to all geometrical variables, using the DFP method included in the MOPAC package of computer programs.[18] The TS were located approximately by the recently developed "saddle" technique,[19] refined by minimizing the norm of the energy,[20] and characterized by establishing that the Hessian (force constant) matrix had one, and only one, negative eigenvalue.[20] From the vibration frequencies and moments of inertia, provided automatically by the force constant program,[18] absolute entropies of molecules and of the TS were calculated by standard methods,[21] using another MOPAC[18] option. Tests[21] have shown that entropies of rigid molecules can be estimated in this way to within 1 eu.

Results

Table I shows the heats of formation (ΔH_f) and entropies (S) calculated for **3**, **4**, and **16–20**, together with experimental values for the former. The agreement is quite good.

Table II shows the calculated values for the enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta H^{\ddagger}$) of activation for the Claisen rearrangements of **3** and **16–20**. Experimental values are included where available, for reactions carried out either in solution in dibutyl ether[22] or in the gas phase.[23]

Figure 1 shows the geometry and ΔH_f calculated for the TS (**11**) for interconversion of **3** and **4**. It has a chair-type geometry, in agreement with the experimental evidence.[7]

Table III compares the bond lengths calculated for **3** and **11**. Note that the breaking CO bond has lengthened only a little in the TS while the forming (C_1C_6) bond is still long. The TS is clearly an "early" one, resembling the reactant in structure, as the evidence from kinetic isotope effects suggests.[14]

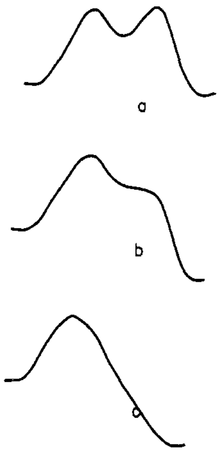

Figure 2. Schematic minimum energy reaction paths (MERPs) for (a) the Cope rearrangement of 1,5-hexadiene and for analogous reactions which are (b) somewhat exothermic and (c) very exothermic.

Discussion

The value of $\Delta H^{\ddagger}$ calculated for **3** → **4** is greater than that observed in the gas phase by 8.9 kcal/mol. This error is not unexpected because MNDO tends to overestimate interatomic repulsions at distances around the van der Waals separation. If the TS in a reaction contains a long weak bond, as is the case in **11**, MNDO will then tend to give too positive an energy for the TS and hence too large an activation energy (enthalpy) for the reaction. The error should not, however, seriously affect comparisons of rates for derivatives of **3**.

The error in $\Delta S^{\ddagger}$ is also larger than usual.[21] Part at least can be attributed to the RRHO (rigid rotor, harmonic oscillator) approximation used in the calculation[21] of entropies. This is known to give values that are too positive for molecules with single bonds about which rotation can take place easily, as is the case for **3** or **4**. Tests[21] have shown that the errors in entropies calculated in this way amount to about 1 eu per C–C single bond. The error may well be somewhat larger for C–O bonds because the barriers to rotation about them are less. Since **3** contains two C–O bonds and one C–C bond, the entropy calculated for it is likely to be too positive by somewhat more than 3 eu. The entropy calculated for the TS (**11**) should not, however, suffer from any such error because **11** is reasonably rigid. The value of $\Delta S^{\ddagger}$ calculated for the Claisen rearrangement of **3** should therefore be too negative, by >3 eu. This could account for the discrepancy between the calculated and observed values. The latter does, however, seem surprisingly small by comparison with entropies of activation reported for Cope rearrangements in the gas phase (see ref 9). Some of the discrepancy may be due to experimental error in the value for **3** which was reported over 30 years ago.

The close formal analogy between the Claisen rearrangement of **3** and the Cope rearrangement of **5** suggests that both reactions are likely to take place by similar mechanisms. The MINDO/3 calculations[10] for **5** → **6**, and the observed[9] effects of phenyl substituents on its rate, indicate that the corresponding MERP (minimum energy reaction path) has the form indicated in Figure 2a, the intermediate minimum corresponding to a biradical species best represented by **10**. Since the rearrangement of **5** to **6** is degenerate, the barriers separating **10** from **5** and from **6** are similar. Consider now the effect of structural changes in **5** that make its conversion to **6** progressively more exothermic (Figure 2b,c). This will lead to a lowering of the energy of the second TS (**10** → **6**) relative to that of the first (**5** → **10**), making the latter the TS for the overall reaction. If the overall reaction becomes sufficiently exothermic, the central minimum in the MERP will disappear (Figure 2c), the reaction becoming concerted[4] although still not synchronous.[4] MNDO indeed predicts the MERP for **3** → **4** to be of this type.

A biradical should be a very polarizable species, because partial or complete transfer of an electron from one radical center to the other can take place without any change in bonding. Indeed, the

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Table II. Enthalpies ($\Delta H^{\ddagger}$) and Entropies ($\Delta H^{\ddagger}$) of Activation for Claisen Rearrangements of 1,5-Hexadienes

	ΔH, kcal/mol		ΔS, cal/mol/K		ΔG, kcal/mol	
	calcd	obsd[a]	calcd	obsd[a]	calcd	obsd[a]
3	39.5	30.6 (g)	−13.4 (453 K)	−7.7 (g 453 K)	45.6	34.1[b]
		25.4 (l)	−12.8 (373 K)	−15.9 (l 373 K)	45.3	31.3[c]
16	39.0		−9.0 (373 K)		42.4	
17	36.6		−8.6 (373 K)		39.8	
18	35.7	22.6 (l)	−12.7 (373 K)	−18.0 (l 373 K)	40.4	29.3[c]
19	38.0	22.8 (l)	−12.9 (373 K)	−13.4 (l 373 K)	42.8	27.8[c]
20	32.1		−12.4 (373 K)		36.7	
21	45.6	27.1 (l)	−13.0 (373 K)	−11.6 (l 373 K)	50.5	31.4[c]
22	38.5	22.3 (l)	−14.6 (373 K)	−13.0 (l 373 K)	43.9	27.1[c]
23	44.4	28.8 (l)	−14.2 (373 K)	−11.2 (l 373 K)	49.7	33.0[c]

[a] g, reaction in the gas phase; l, reaction in di-*n*-butyl ether solution. [b] Reference 23. [c] Reference 22.

Table III. Bond Lengths in Transition States and Reactants[a]

	C_1–C_2	C_2–C_3	C_3–O	O–C_5	C_5–C_6	C_6–C_1
3	1.40 (1.34)	1.48 (1.52)	1.46 (1.41)	1.34 (1.37)	1.41 (1.35)	1.88 (4.47)
16	1.41 (1.35)	1.50 (1.54)	1.45 (1.41)	1.34 (1.37)	1.41 (1.35)	1.90 (4.55)
17	1.39 (1.34)	1.48 (1.52)	1.46 (1.41)	1.34 (1.37)	1.42 (1.35)	1.93 (4.15)
18	1.41 (1.35)	1.50 (1.53)	1.45 (1.40)	1.34 (1.37)	1.41 (1.35)	1.93 (4.45)
19	1.40 (1.34)	1.49 (1.51)	1.45 (1.41)	1.35 (1.37)	1.42 (1.35)	1.88 (4.23)
20	1.40 (1.35)	1.50 (1.53)	1.45 (1.41)	1.34 (1.37)	1.41 (1.35)	2.01 (4.11)
21	1.41 (1.34)	1.48 (1.51)	1.46 (1.41)	1.33 (1.36)	1.43 (1.36)	1.84 (5.24)
22	1.40 (1.34)	1.49 (1.53)	1.47 (1.41)	1.34 (1.37)	1.41 (1.35)	1.89 (4.72)
23	1.41 (1.34)	1.48 (1.52)	1.46 (1.40)	1.33 (1.37)	1.42 (1.35)	1.86 (5.12)

[a] Bond lengths in Å; values for reactants in parentheses.

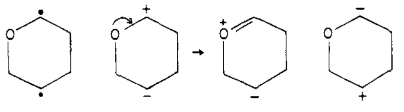
Table IV. Charge Distributions in Transition States and Reactants[a]

	C_1	C_2	C_3	O	C_5	C_6
3	0.06 (−0.04)	−0.27 (−0.16)	0.20 (0.22)	−0.27 (−0.29)	0.07 (0.06)	−0.09 (−0.11)
16	0.03 (−0.07)	−0.10 (0.0)	0.19 (0.21)	−0.27 (−0.29)	0.05 (0.06)	−0.07 (−0.11)
17	0.09 (−0.03)	−0.33 (−0.16)	0.22 (0.22)	−0.30 (−0.31)	0.26 (0.20)	−0.12 (−0.10)
18	0.12 (0.03)	−0.25 (−0.09)	0.23 (0.23)	−0.27 (−0.28)	0.15 (0.05)	−0.14 (−0.10)
19	0.01 (−0.03)	−0.19 (−0.17)	0.18 (0.21)	−0.25 (−0.28)	0.08 (0.12)	−0.01 (−0.02)
20	0.15 (0.03)	−0.29 (−0.10)	0.25 (0.24)	−0.31 (−0.31)	0.32 (0.19)	−0.17 (−0.09)
21	0.09 (−0.03)	−0.30 (−0.17)	0.21 (0.21)	−0.26 (−0.28)	0.13 (0.15)	−0.04 (−0.09)
22	0.06 (−0.02)	−0.27 (−0.14)	0.30 (0.31)	−0.27 (−0.28)	0.08 (0.05)	−0.08 (−0.09)
23	0.13 (0.00)	−0.25 (−0.08)	0.20 (0.21)	−0.26 (−0.28)	0.08 (0.05)	−0.08 (−0.11)

[a] Charges in units of the electronic charge; values for reactants in parentheses

"sudden polarization effect"[24] corresponds to such a polarization of the biradical intermediate involved in rotation about a C=C bond. The same should also be true to a lesser extent for biradicaloids where there is some interaction between the radical centers, leading to stabilization that is lost in the corresponding zwitterion (e.g., **12** from **10**). Since a $+E$ substituent, i.e., an electron withdrawing conjugative substituent such as CN, NO_2, or RCO, stabilizies a carbanion more strongly than it does the corresponding radical, and since a $-E$ (electron releasing conjugative) substituent (CH_3O, H_2N, etc.) likewise stabilizes a carbenium ion more strongly than it does the corresponding radical, introduction of a $+E$ or $-E$ substituent at a radical center in a biradical or biradicaloid should stabilize it strongly, the biradical polarizing in such a way as to maximize its interaction with the substituent. Furthermore, mutual conjugation[25,26] between a $+E$ substituent at one radical center and a $-E$ one at the other should lead to especially strong stabilization, both substituents cooperating in polarizing the biradical. Electromeric substituents at C_2 or C_5 do indeed accelerate the Cope rearrangement of **5**, while double substitution, by a $+E$ substituent at one position and a $-E$ one at the other, leads to a very large increase in rate.[27]

A similar situation should hold in the case of the Claisen rearrangement of **3** except that here the oxygen atom is attached to one radical center in the intermediate biradical (**13**). The $-E$ effect of the oxygen should then favor polarization in the sense **13** → **14** rather than **13** → **15**. A $-E$ substituent should therefore increase the rate of the Claisen rearrangement of **3** more at C_5 than at C_2 while $+E$ substituent should increase the rate more at C_2 than at C_5. Also, since the TS occurs earlier in the reaction than it does in the Cope rearrangement of **5**, less cooperation might be expected between substituents of opposite types in the 2- and 5-positions.



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Calculations were therefore carried out for the 2- (**16**) and 5- (**17**) methoxy, 2- (**18**) and 5- (**19**) cyano, and 2-methoxy-5-cyano derivatives of **3**. As Table II shows, *all* were predicted to rearrange more rapidly than **3** itself. The acceleration by methoxy ($-E$) is moreover predicted to be greater at C_5 than at C_2 while the reverse is predicted for cyano ($+E$). Furthermore, the acceleration by methoxy at C_5 is predicted to be much greater than that by cyano, while the reverse is true at C_2. All these results agree with the predictions made above.

Burrows and Carpenter[22] have reported kinetic data for the rearrangements of **3**, **18**, and **19**, and also for the additional cyano derivatives **21**–**23**, in dibutyl ether solution. Their results for **21**–**23** are included in Table II. The rates for **18** and **19** were greater than that for **3**, in agreement with our arguments and calculations. However, while we predict **18** to rearrange twenty times faster than **19** at 400 K, the observed rate was eight times less. The

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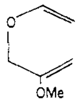

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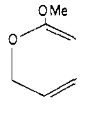

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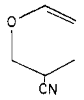

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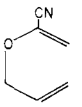

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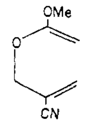

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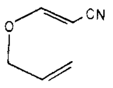
observed differences in rate between **3** and **18** or **19** are also less than those calculated. Comparison with our calculations is unfortunately complicated by the presence of a rather large solvent effect, indicated by the data for **3** in Table II. It is unfortunate that no data are available for compounds with methoxy substituents.



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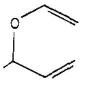

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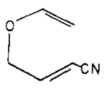

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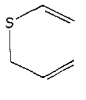
The cyano group in **22** moves into conjugation with a double bond during the rearrangement while the cyano groups in **21** and **23** move out of conjugation. **22** should therefore rearrange faster than **3** while **21** and **23** should rearrange more slowly. This is what was observed.[22] Calculations were not carried out initially for these reactions because it seemed certain that *any* procedure would reproduce the relative rates qualitatively while quantitative agreement could not be expected in view of the demonstratedly large effect of the solvent. When calculations for the rearrangements of **21**–**23** were later carried out at the insistence of a referee, the results (Table II) confirmed our expectations.

There is an obvious need for more kinetic data, in particular for derivatives of **3** containing $-E$ (e.g., methoxy or dimethylamino) substituents and for species such as **20** with a $-E$ substituent in the 2-position and a $+E$ one in the 4-position. Studies of the latter would be particularly interesting because our calculations, together with the rates measured for **3**, indicate that **20** should rearrange at a measurable rate at room temperature, the half-life being about 14 h.

Similar accelerations have been observed in the hetero-Cope rearrangements of allyl vinyl sulfides[28] (**24**) and imines[29] (**25**). All these reactions seem to involve definite polar intermediates, seemingly of 1,4-dipolar type. As noted earlier, neither our calculations nor the experimental evidence provide any evidence for the intervention of such intermediates in the Claisen rearrangement of **3**.



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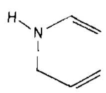

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Symmetry of MNDO Transition States

Some years ago Houk et al.[30] presented arguments supporting the thesis that in reactions where two bonds are formed or broken, MINDO/3 and MNDO erroneously predict unsymmetrical transition states in which the lengths of two bonds are unequal. While their arguments have been rebutted in print,[31] many chemists are clearly unaware of the rebuttal. Since the matter is clearly of major importance and since their paper has been widely quoted, further discussion seems in order.

Houk et al. based their arguments (a) on papers by Townsend et al.[32] and Burke et al.[33] reporting ab initio calculations for the Diels–Alder reaction between ethylene and 1,3-butadiene; (b) on a paper by Poppinger[34] reporting similar calculations for the dipolar addition of fulminic acid to acetylene; (c) on a comparison of results from an EH calculation for the ethylene–butadiene reaction with those from a similar treatment neglecting overlap; and (d) on theoretical considerations based on a rather simplistic model.

(a) No conclusions can in fact be drawn from the calculations[32,33] for the ethylene–butadiene reaction because numerous geometrical assumptions were made,[35] because the remaining geometrical parameters were not optimized properly,[36] because the claimed "transition state" was not demonstrated to be a stationary point on the potential surface, let alone characterized as a transition state,[37] and because no attempt was made to locate an unsymmetrical TS of lower energy than that of the claimed symmetrical one.[38] As we have emphasized repeatedly over the last 10 years, studies of reactions are worthless if the precautions implied above are not taken, regardless of the accuracy of the theoretical procedure used.

(b) Poppinger[34] was in fact the first to carry out an adequate ab initio study of an organic reaction, i.e., the dipolar addition of acetylene to fulminic acid. He concluded that the TS is symmetrical because the lengths of the forming CC and CO bonds were found to be equal. While Poppinger used a poor[40] ab initio model (STO-3G), a reexamination of the reaction by Komornicki et al.,[41] using a "state-of-the-art" ab initio procedure, led to similar results. Komornicki et al., however, also calculated stretching force constants for the forming CC and CO bonds in the TS. The values found (3.07 and 0.31 mdyn/Å, respectively) show that while the CC bond is already strong, the force constant being more than half that of a normal C–C bond, the CO bond is still extremely weak. The TS is therefore in fact *very unsymmetrical*, the CO bond having hardly begun to form. The lengths of the CC and CO bonds are nevertheless almost the same because the C–O single bond is shorter and stiffer than C–C. At their lengths in the TS (2.19 and 2.21 Å, respectively), a CC bond is still strong while a CO bond has almost ceased to exist.

(c and d) Both these arguments are weak, given the known inadequacy[42] of the EH method and the highly simplified treatment used[30] to deduce the effect of overlap. However, even if the conclusion were correct, it would be irrelevant to the situation in MINDO/3 or MNDO. These treatments were parametrized to reproduce experimental observations, i.e., to mimic the exact solutions of the Schrödinger equation that Nature has provided.[43] The fact that they give good estimates of ground-state properties of all kinds, for molecules of all kinds,[44] including properties and

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(28) Gompper, R.; Ulrich, W. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 301.

(29) Gompper, R.; Kohl, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 198.

(30) Caramella, P.; Houk, K. N.; Domelsmith, L. N. *J. Am. Chem. Soc.* **1977**, *99*, 4511.

(31) Dewar, M. J. S.; Olivella, S.; Rzepa, H. C. *J. Am. Chem. Soc.* **1978**, *100*, 5650.

(32) Townsend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190.

(33) Burke, L. A.; Leroy, J.; Sana, M. *Theor. Chim. Acta* **1975**, *40*, 313.

(34) Poppinger, D. *J. Am. Chem. Soc.* **1975**, *98*, 7486; *Aust. J. Chem.* **1976**, *29*, 465.

(35) Any geometrical assumption concerning the structure of the TS of a reaction is equivalent to an assumption concerning its mechanism. Calculations based on such assumptions tend to reproduce the mechanisms tacitly assumed.

(36) Cyclic variation of coordinates is not an acceptable optimization procedure, as indeed is now generally recognized.

(37) It is particularly necessary to characterize a symmetrical TS by calculating force constants[20] because methods for locating TS can easily mistake the top of a hill for a saddle point.

(38) Townsend et al.[32] found a biradical-like minimum on the potential surface but failed to find the paths leading to and from it.

(39) The errors in energies calculated by the STO-3G model are, on average, several times greater than those from MNDO.[40]

(40) See: (a) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 5558. (b) Dewar, M. J. S.; Storch, D. M. *J. Am. Chem. Soc.*, submitted for publication.

(41) Komornicki, A.; Goddard, J. D.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 1763.

(42) The EH model, inter alia predicts neither H_2 nor benzene to exist, the former collapsing to He^2 and the latter dissociating exothermically and without activation to acetylene; see ref 40a.

(43) Assuming of course that exact solutions of the Schrödinger equation would reproduce nature with "chemical accuracy", which is by no means certain.

types of molecule not used in determining the parameters, indicates that the parametrization is doing a remarkably good job at coping with the deficiencies of what are admittedly extremely crude approximations to the Schödinger equation. The neglect of overlap in the INDO and NDDO approximations is clearly one of the worst of these deficiencies. The implication is that it is adequately compensated in MINDO/3 and MNDO. Indeed, if the effects of overlap could be allowed for in these treatments without making any other changes, the implication from Houk's work is that they would then *overestimate* the stabilities of symmetrical structures.

If the tendency to make transition states unsymmetrical were universal, or if some predictions of unsymmetrical ones were contrary to the experimental evidence, the situation would of course be different, but this is not the case. Both MINDO/3 and MNDO *do* predict symmetrical transition states in many reactions where unsymmetrical structures would be perfectly feasible, e.g., various ene reactions,[45] and the experimental evidence in other cases is fully consistent with the unsymmetrical structures predicted by MINDO/3 and/or MNDO.[46]

No current theoretical procedure is reliable, and no claims to the contrary could be, or have been, made for MINDO/3 or MNDO. However, attempts to refute conclusions drawn from them, if based on inadequate calculations or specious arguments, are not helpful. What is needed in the present connection is more experimental data and/or a high-level ab initio calculation for the rearrangement of **3**, of the kind reported by Komornicki et al. for the ethylene–fulminic acid cycloaddition.[41]

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract F49620-83-C-0024) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out on a VAX 11-780 computer provided by grants from the National Science Foundation (Grant CHE82-17948) and The University of Texas at Austin.

Registry No. 3, 3917-15-5; **4**, 2100-17-6; **16**, 92127-02-1; **17**, 92127-03-2; **18**, 92127-04-3; **19**, 60838-52-0; **20**, 92127-05-4; **21**, 60838-49-5; **22**, 79929-67-2; **23**, 79999-08-9.

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(44) Even including positive[27] and negative[45] ions and radicals.[27]

(45) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 784.

(46) See e.g.: Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 8343.

(47) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

A Novel Organic Photochromic

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Contribution from the Institute for Polymers and Organic Solids, Department of Physics, University of California, Santa Barbara, California 93106, and The J. D. Mc Cullough X-ray Crystallography Laboratory, Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. Received April 10, 1984

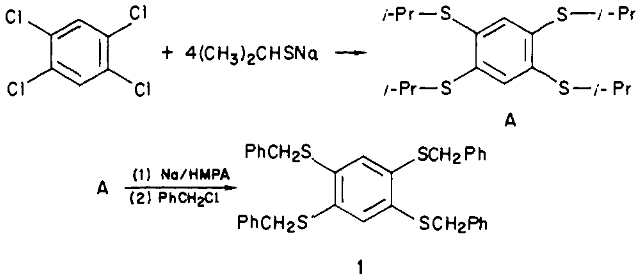
Abstract: Irradiation of 1,2,3,4-tetrakis(benzylthio)benzene with ultraviolet or visible light changes its color from white to dark pink; heating the irradiated sample above $\simeq$80 °C reverts its color to white. It was determined that this phenomenon is due to a solid-state process. Attempts to establish, unambiguously, a mechanism for photochromism were unsuccessful. The X-ray structure determination of the molecular structure of this photochromic material as well as the mode of packing with emphasis on possible intermolecular as well as intramolecular interactions are described.

Photochromic compounds have been studied since the end of the last century in a more or less sporadic manner[1] but have become the subject of very active research in the more recent past because of their potential as photostorage devices.[2]

As part of a different project, was needed to prepare 1,2,4,5-tetrakis(benzylthio)benzene (**1**) as a logical precursor for the preparation of the corresponding benzene-1,2,4,5-tetrathiol[3] via solvated electron reduction.[3] Much to our surprise, a survey of the literature revealed that whereas a number of 1,2,4,5-tetrakis(alkylthio)benzenes had been prepared,[3] compound **1** was unknown. In Scheme I we show how the desired product was obtained.

The reactions in this approach are based mainly on work described in ref 3. At first sight it would appear that one could have prepared **1** directly from a tetrahalobenzene and benzylmercaptide. Unfortunately, under the conditions required for nucleophilic aromatic substitution (polar aprotic solvent, elevated temperature), debenzylation takes place[4] concomitant with nucleophilic substitution. Previous work showed this to be the case also when methyl mercaptide was used as the nucleophile.[3]

Scheme I



Compound **1** is a white, crystalline solid[5] which quickly turns pink when exposed to light, either fluorescent or solar. It can be shown, as follows, that this change in color is due to a solid-state process: 1. The infrared spectrum of a KBr pellet before and

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[‡] University of California, Los Angeles.

(1) Exelby, R.; Grinter, R. *Chem. Rev.* **1965**, *65*, 247. DoMinh, T.; Trozzolo, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 4046.

(2) Brown, G. H., Ed. "Photochromism"; Wiley-Interscience: New York, 1971; Vol. 3.

(3) Preparation of A: Testaferri, L.; Tingoli, M.; Tiecco, M. *J. Org. Chem.* **1980**, *45*, 4376. Reduction of A to a claimed yield of 63% of benzene-1,2,4,5-tetrathiol (in our hands a yield of tetrathiol of, at best, 10%): Maiolo, F.; Testaferri, L.; Tiecco, M.; Tingoli, M. *J. Org. Chem.* **1981**, *46*, 3070. Reduction of tetrakis(alkylthio)benzenes with alkali metals: Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Radebaugh, R. K. *Phosphorus Sulfur* **1982**, *13*, 309.