correlation energy.[33] Since the error commonly amounts to 15–20 kcal/mol, the minima in the reaction profiles of Figures 3, 8, and 12 are probably not real. A similar situation arose in the case of the Diels–Alder reaction between **2** and **20**, as was pointed out at the time.[21] This error will naturally tend to make the transition states leading to such species too unsymmetric, but there are reasons for believing that the conclusions reached here concerning their structures are nevertheless essentially correct.

In the first place, very similar structures for the TS were predicted by the usual spin-unrestricted versions of MINDO/3 and MNDO (Figures 2, 7, 11, 15) although these grossly overestimate the energies of biradical-like species. This indeed is why these methods give activation energies that are far too large. There is, moreover, no indication of any systematic errors, either in MINDO/3 or in MNDO, that might be expected to make them overestimate the energy of a symmetrical TS relative to that of an analogous unsymmetrical one.[34] Both MINDO/3 and MNDO have indeed predicted symmetrical TS for several other pericyclic reactions.[37]

Secondly, the reasonable agreement between the calculated entropies of activation, both here and for the Diels–Alder reaction of **2** with **20**,[21] provide good support for the predicted TS structures.

And finally, McIver's rules[38] predict all these reactions to take place via transition states that are unsymmetrical. While these rules cannot indicate the extent to which symmetry is broken in any given case, and while their application to cycloaddition reactions is not completely rigorous,[39] they do nevertheless provide a strong indication that such processes cannot be synchronous.[20]

There seems, therefore, to be a strong indication that the cheletropic reactions considered here are not synchronous processes, as had been commonly assumed because they are "allowed" by the Woodward–Hoffman rules.[3] On the contrary, they seem to proceed via TS which are very unsymmetrical, one of the two breaking bonds being still almost intact while the other is weak.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 79-0008) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out using a Digital Vax 11/780 computer provided by grants from the National Science Foundation (Grant CHE78-03213) and The University of Texas, and the Dual Cyber 170/750 computer at The University of Texas Computation Center.

Registry No. 1, 87494-91-5; **10**, 87494-92-6; **12**, 930-30-3; **17**, 826-65-3.

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(33) See, e.g.: Dewar, M. J. S.; McKee, M. L. *Pure Appl. Chem.* **1980**, *52*, 1432.

(34) For a refutation of claims to the contrary by Caramella et al.,[35] and of a much quoted ab initio study by Townshend et al.,[36] see ref 21.

(35) Caramella, P.; Houk, K. N.; Domelsmith, L. N. *J. Am. Chem. Soc.* **1977**, *99*, 4514.

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

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

(38) McIver, J. W. *J. Am. Chem. Soc.* **1975**, *97*, 3632.

(39) In this case the argument rests on the assumption that off-diagonal force constants are always smaller than corresponding diagonal ones. While this is certainly true for stable molecules, it might not be for transition states.

Ground States of Molecules. 63. Reverse Cheletropic Reactions in Polycyclic Systems

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Abstract: MINDO/3 and MNDO calculations are reported for the reverse cheletropic decarbonylations of 7-norbornenone, 7-norbornadienone, and *exo*- and *endo*-tricyclo$[4.1.0.1^{2,5}]$oct-3-en-8-one, and the reverse cheletropic denitrigenation of 1,4-cyclohexadien-2,5-ylene-1,1-diazene. The first four reactions are predicted to take place in a nonsynchronous manner via very unsymmetrical transition states while the last is synchronous, or almost synchronous.

Introduction

Our previous paper[2] reported MINDO/3[3] and MNDO[4] calculations for a number of reverse cheletropic reactions involving loss of CO or N_2 from unsaturated five-membered rings to form derivatives of 1,3-butadiene. Here we describe similar calculations for the reverse cheletropic loss of N_2 or CO from 7-norbornenone, the corresponding diazene, and various analogues containing additional structural features. Full details of the procedure used were given in the previous paper[2] and need not be repeated here.

Results and Discussion

The calculations for the individual compounds will first be considered in turn, the results being compared with experimental data when these are available. The final section discusses the collective implications of this work concerning the mechanisms of cheletropic reactions in general.

A. 7-Norbornenone (1). The first reaction studied was the thermolysis of 7-norbornenone (**1**) to 1,3-cyclohexadiene (**2**) and carbon monoxide (**3**).

Table I compares various properties calculated by MINDO/3 and MNDO for **1** with experimental values, where available. The agreement is acceptable. Since the energies calculated by MINDO/3 for norbornane and norbornadiene are much too positive,[3] whereas those from MNDO agree quite well with experiment,[4]

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(1) For part 60 see: Dewar, M. J. S.; Nelson, D. J. *J. Org. Chem.* **1982**, *47*, 2614.

(2) Dewar, M. J. S.; Chantranupong, L. *J. Am. Chem. Soc.*, preceding paper in this issue.

(3) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302.

(4) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907.

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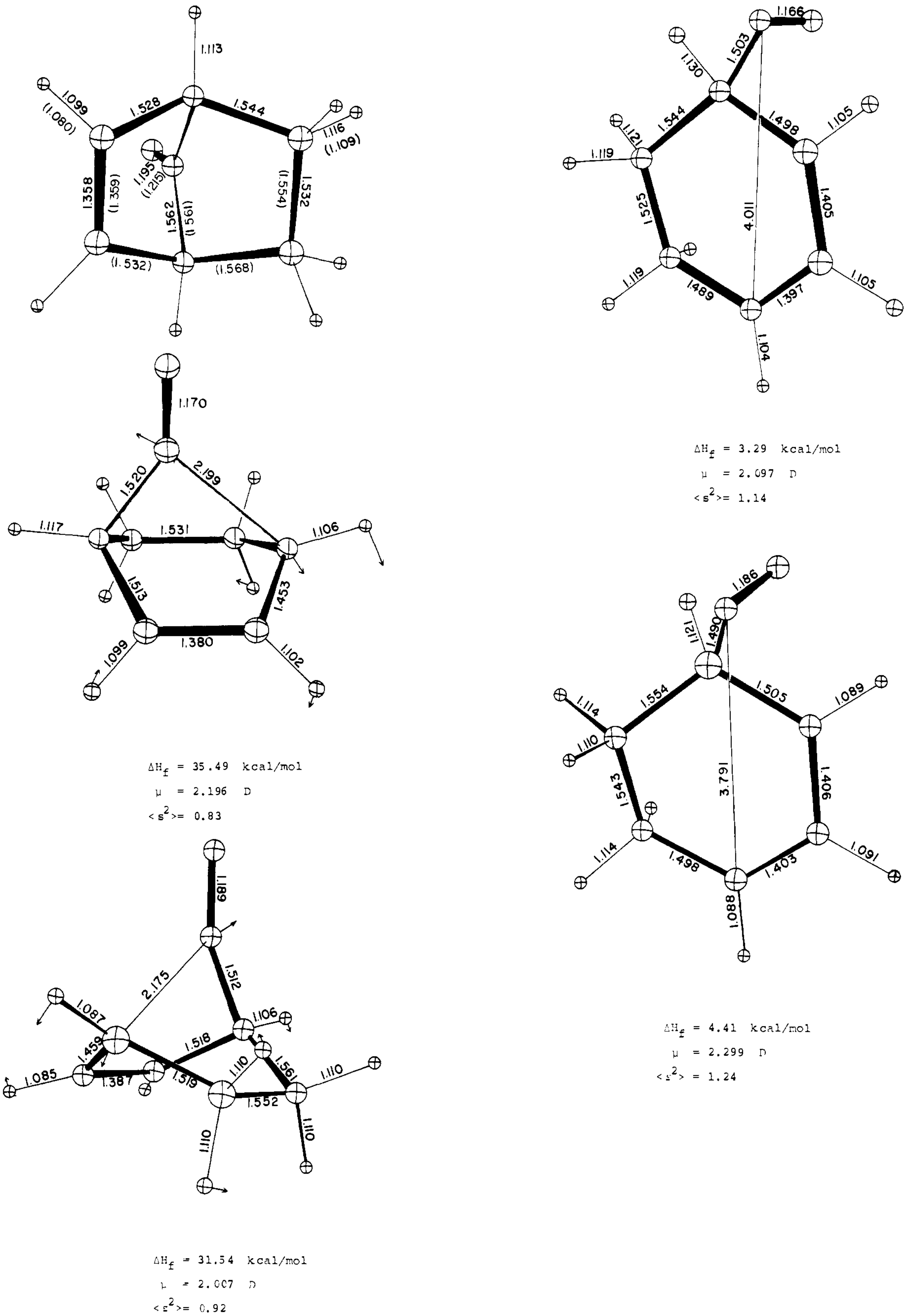


Figure 1. Geometries and other properties calculated (a) for 7-norbornenone (**1**) by MINDO/3 (MNDO); (b)(c) the first TS; (d)(e) the intermediate: (b)(d) MNDO; (c)(e) MINDO/3.

the MNDO value for **1** is probably nearer the truth.

Figure 1a shows the geometries calculated for **1** by MINDO/3 and MNDO. They agree closely. While no experimental structure is available for comparison, both lead to moments of inertia in good agreement with experiment (Table I).

MINDO/3 and MNDO predict the conversion of **1** to (**2** +

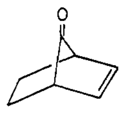
Table I. Various Properties Calculated by MINDO/3 and MNDO for 1

method (molecule)	ΔH_f (kcal/mol)	IP (eV)	μ (D)	moment of inertia (amu A^2)		
				I_a	I_b	I_c
MINDO/3 (1)	11.96	9.354	2.87	173.050	210.190	229.558
MNDO (1)	3.95	10.11	2.49	171.670	214.264	232.495
obsd			2.91[a] ± 0.04[a]	169.639[a]	208.960[a]	226.070[a]

[a] Durig, J. R.; Lopata, A. D.; Li, Y. S. *J. Mol. Struct.* 1975, *26*, 85.

3) to be slightly exothermic, and calculated heats of reaction being respectively −19.6 and −16.0 kcal/mol. While no experimental data are available for comparison, the reaction certainly takes place much more readily than the corresponding elimination of **3** from 3-cyclopentenone (**4**) to form butadiene (**5**), which is strongly endothermic, the heats of reaction (ΔH) calculated by MNDO and MINDO/3 being 29.2 and 30.6 kcal/mol, respectively. The difference between the two reactions can of course be attributed to relief of angle strain in the case of **1**.

The conversion of **1** to (**2** + **3**) was first studied by the usual RHF versions[3,4] of MINDO/3 and MNDO, taking the length of a breaking CC bond as the reaction coordinate.[5] It soon became apparent that the reaction involved biradical-like intermediates because the activation energies found in this way were very large. This indeed was to be expected by analogy with the conversion[1] of **4** to (**5** + **3**). The calculations were therefore repeated, using the UHF (spin-unrestricted) versions of MINDO/3 (UMINDO/3[6]) and MNDO (UMNDO[7]). Both methods predicted the reaction to take place in steps[8] via a biradical (**6**) as a stable intermediate. Figures 1b and 1c show the structure calculated for the transition states (TS) and Figure 1d and 1e those for the intermediate. Here, and subsequently, the arrows in figures depicting TS denote the corresponding transition vector,[5] i.e., the relative magnitudes and directions of motion of the individual atoms in the normal mode which has a negative force constant (transition coordinate[5]). Transition coordinates are calculated routinely in our use of McIver–Komornicki[9] procedure[10] to characterize stationary points on a potential surface, in particular, those corresponding to TS.



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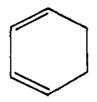

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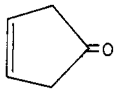

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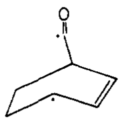

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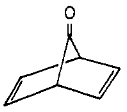

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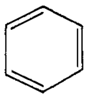

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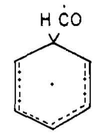

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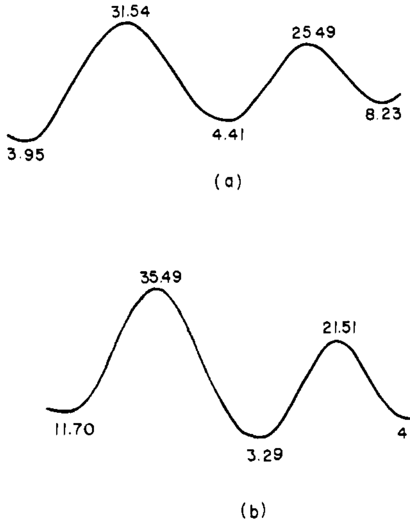

Figure 2. Reaction profiles for the thermolysis of **1** calculated (a) by MNDO; (b) by MiNDO/3.

Table II. Activation Parameters for Thermolysis of 1

method	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)	log A
MNDO	27.59	3.48	13.99
MINDO/3	23.79	1.21	13.49
obsd[13]	30.10 ± 1.70	−4.40 ± 4.40	

Figure 2 shows the overall reaction profiles for the decarbonylation of **1**. Note that the rate-determining step for the overall reaction is breaking of the first bond in **1** to form **6**.

UMINDO/3 and UMDO are known[11] to overestimate the stabilities of singlet biradicals and biradical-like species because of an overestimation of their correlation energies. The available evidence[12] suggests that the corresponding error in the calculated ΔH_f is 15–20 kcal/mol. Since the barrier separating **6** from (**2** + **3**) is less than this, the conversion of **6** to (**2** + **3**) may, in fact, take place without activation. The overall conversion of **1** to (**2** + **3**) would then be concerted.[8] Our calculations do, however, indicate very strongly that it is not synchronous,[8] taking place via a very unsymmetrical TS where one of the breaking CC bonds is essentially intact (Figures 1c,d). This point will be discussed in more detail in the final section of this paper.

Table II compares with experiment[13] the calculated enthalpies ($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$) of activation for the thermolysis of **1**. The agreement is satisfactory, being well within the range of error expected for MINDO/3 or MNDO. Both methods give values for $\Delta H^\ddagger$ that are too small because of their overestimation of the stability of **6**. However, the bond lengths calculated for the TS (Figures 1b,c) do not indicate any extensive biradical character in it, and this was confirmed by single RHF calculations of its energy, using the UHF geometry. The values found in this

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(5) The term "reaction coordinate" is used here in its original sense, i.e., to denote an arbitrary geometrical variable whose value changes during a reaction and which can therefore be used to follow its progress. The normal coordinate with a negative force constant in a TS is described here as the *transition coordinate*. See ref 2.

(6) Bischof, P. *J. Am. Chem. Soc.* **1976**, *98*, 6844.

(7) Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *Chem. Phys. Lett.* **1977**, *47*, 80. Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 784.

(8) See ref 20 in preceding paper.[2]

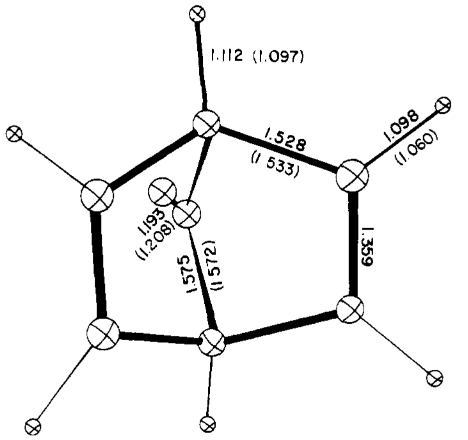
(9) McIver, J. W., Jr.; Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

(10) McIver, J. W., Jr.; Komornicki, A. *Chem. Phys. Lett.* **1971**, *10*, 303.

(11) Dewar, M. J. S.; McKee, M. L. *Pure. Appl. Chem.* **1980**, *92*, 1432.

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

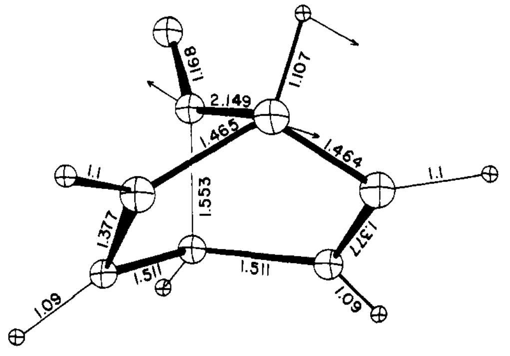
(13) Clarke, S. C.; Johnson, B. L. *Tetrahedron.* **1971**, *27*, 3556.; "Symmetry"; Academic Press: New York, 1972.



ΔH_f = 43.23 (33.67) kcal/mol

IP = 9.288 (9.941) ev

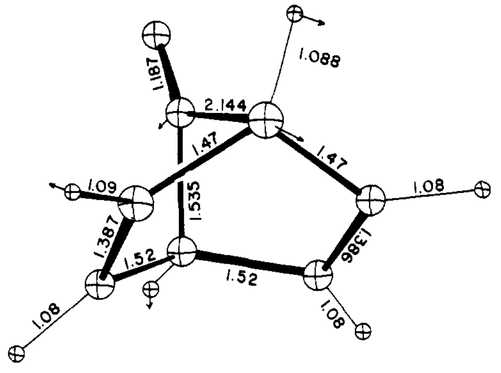
μ = 2.755 (2.325) D



ΔH_f = 65.71 kcal/mol

μ = 1.897 D

$\langle s^2 \rangle$= 0.76



ΔH_f = 60.34 kcal/mol

μ = 1.767 D

$\langle s^2 \rangle$= 1.09

Figure 3. Geometries and other properties calculated (a) for 7-norbornadienone (7) by MINDO/3 (MNDO); (b)(c) the TS for conversion of 7 to 9. (b) MINDO/3; (c) MNDO.

way (MNDO, 8.7; MINDO/3, 9.6 kcal/mol) were only a little greater than the UHF ones.

B. 7-Norbornadienone (7). The conversion of 7-norbornadienone (7) to benzene (8) and 3 followed a course similar to that of 1 to (2 + 3). It likewise involved biradical-like intermediates and so also had to be studied using UMINDO/3 and UMNDO.

Figure 3a shows the geometries and other properties calculated for 7. No experimental data are available for comparison. As noted earlier,[11] UMINDO/3 and UMNDO lead to the closed-shell solutions for **8**, reported previously.[3,4] The corresponding heats of reaction were −38.9 (MINDO/3) and −40.8 (MNDO) kcal/mol, indicating the reaction to be strongly exothermic. This difference from **1** is of course due to the formation of an aromatic product (**8**). The difference between the calculated heats of reaction is indeed close to the aromatic stabilization energy (ASE) of benzene (21 kcal/mol[12]).

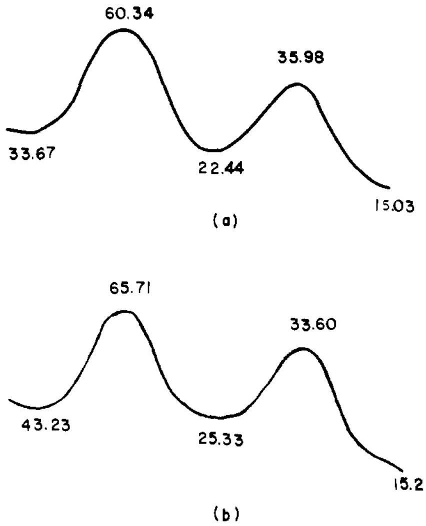


Figure 4. Reaction profiles for the thermolysis of 7, calculated (a) by MNDO; (b) by MINDO/3.

Table III. Activation Parameters for Thermolysis of 7

method	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	log A
MINDO/3	22.48	3.50	13.99
MNDO	26.67	3.46	13.98

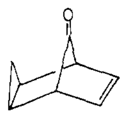
Figure 4 shows the calculated reaction profiles for the overall conversion of **7** to (**8** + **3**). As in the case of **1**, the rate-determining step is the formation of a biradical (**9**) as a stable intermediate, via a very unsymmetrical TS. The structure calculated for the TS are shown in Figures 3b and 3c.

Here again the ΔH_f's calculated for the intermediate (**9**) are expected to be too negative by 15–20 kcal/mol. Since this is greater than the barrier separating **9** from the products (**8** + **3**), it seems likely that the thermolysis of **7** is also a one-step[8] concerted[8] process. However, the prediction that the TS leading to it, and hence the TS for the overall reaction, is very unsymmetric, still stands. In it one of the breaking bonds is still intact while the other is very long (Figures 3b,c). The structure calculated for **9** are not reproduced because they presented no unexpected features and are in any case of doubtful significance.

Table III shows the activation parameters calculated for thermolysis of **7**. They imply that the reaction should be a little easier than that of **1**, owing no doubt to the fact that the intermediate biradical (**9**) has a larger resonance energy than **6**, **9** being a pentadienyl radical while **6** is only an allyl radical. No experimental value is available for comparison, but the qualitative evidence shows that **7** not only decomposes faster than **1** but very much faster.[13] The difference is undoubtedly far greater than our calculations would imply. This discrepancy will be discussed in detail in the final section.

C. *exo*- (10) and *endo*- (11) Tricyclo[4.1.0.1^{2,5}]oct-6-en-8-one. The next compounds studied, *exo*- (**10**) and *endo*- (**11**) tricyclo[4.1.0.1^{2,5}]oct-6-en-8-one, are stereoisomers derived by replacement of one of the double bonds in **7** by a cyclopropane ring. Thermolysis of either **10** or **11** leads to 1,3,5-cycloheptatriene (**12**) and **3**, the cyclopropane ring opening during the reaction. Table IV compares properties calculated by MINDO/3 and MNDO for **10** and **11**. As before, the MNDO values are probably closer to the truth. The geometries of **10** and **11** are not reproduced because, except for the cyclopropane rings, they are similar to that of **1**. The lengths of the bonds in the cyclopropane rings, given by MINDO/3 (MNDO), were:

$$\begin{aligned} &\mathbf{10}\ \mathrm{H_2C{-}CH},\ 1.505\ (1.530);\ \mathrm{HC{-}CH},\ 1.558\ (1.559) \\ &\mathbf{11},\ \mathrm{H_2C{-}CH},\ 1.503\ (1.524);\ \mathrm{HC{-}CH},\ 1.566\ (1.577) \end{aligned} \qquad (1)$$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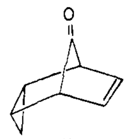
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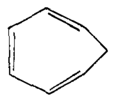
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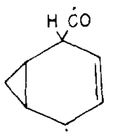
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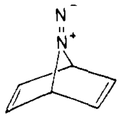
14

N≡N

15

The conversions of **10** and **11** to (**12** + **3**) followed a course similar to those of **1** to (**2** + **3**) and **7** to (**8** + **3**), involving biradical intermediates and having therefore to be studied using UMINDO/3 or UMNDO. The corresponding reaction profiles are shown in Figure 5. The rate-determining step in each case is again the formation of a biradical-like intermediate (**13**). Figures 6a–d show the geometries and other properties calculated for the corresponding transition states. In each case the predicted barrier to conversion of the intermediate to (**12** + **3**) is again low enough for it to be doubtful whether the intermediate in fact corresponds to a local minimum on the potential surface. The structures calculated for it are therefore not reproduced.

Table V compares with experiment[13] activation parameters calculated for the two reactions by MINDO/3 and MNDO. The agreement for the exo isomer (**10**) is good, and both procedures correctly predict this reaction to take place more easily than that of **1**. Both methods also correctly predict the endo isomer (**11**) to be more reactive than **10**, but both greatly underestimate the difference in rate between the two reactions. This suggests that the thermolysis of **11** may be assisted by concerted opening of the three-membered ring. Since both MINDO/3 and MNDO predict the ring opening to take place after the rate-determining step, in both **10** and **11**, they would then underestimate the relataive rate of thermolysis of **11**.

This suggestion is strongly supported by the calculated and observed entropies of activation ($\Delta S^{\ddagger}$). While both UMINDO/3 and UMDO predict all four to be approximately equal and while the experimental values for **1** and **10** agree quite well with the calculations, the experimental value for **11** is much more positive, as would be expected if the rate-determining step in this case alone involved opening of an additional ring.

This error presumably reflects once more the tendency of both methods to overestimate the stabilities of biradicals, in particular, that (**13**) generated by breaking of a C–CO bond in **10** or **11**. Opening of the three-membered rring in **13** is consequently predicted to require activation, preventing the overall reaction from taking place in a concerted manner. The error in the case of **10** is not significant because its geometry is such as to inhibit participation by the ring. Problems arise, however, in the case of **11** where the orbital geometry favors participation.

Table IV. Properties Calculated for 10 and 11 by MINDO/3 and MNDO

method (molecule)	ΔH_f (kcal/mol)	IP (eV)	μ (D)
MNDO (10)	36.85	10.118	2.471
MINDO/3 (10)	45.57	9.103	3.027
MNDO (11)	37.81	10.126	2.442
MINDO/3 (**11**)	45.84	9.130	2.797

Table V. Activation Parameters for Thermolysis of 10 and 11

method (molecule)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	log A
MNDO (10)	32.00	1.84	13.63
MINDO/3 (10)	26.71	1.19	13.49
obsd[13] (**10**)	31.60 ± 1.90	−3.60 ± 4.60	
MNDO (**11**)	31.80	2.27	13.72
MINDO/3 (11)	24.52	1.29	13.51
obsd[13] (11)	25.50 ± 0.70	6.00 ± 2.40	14.50

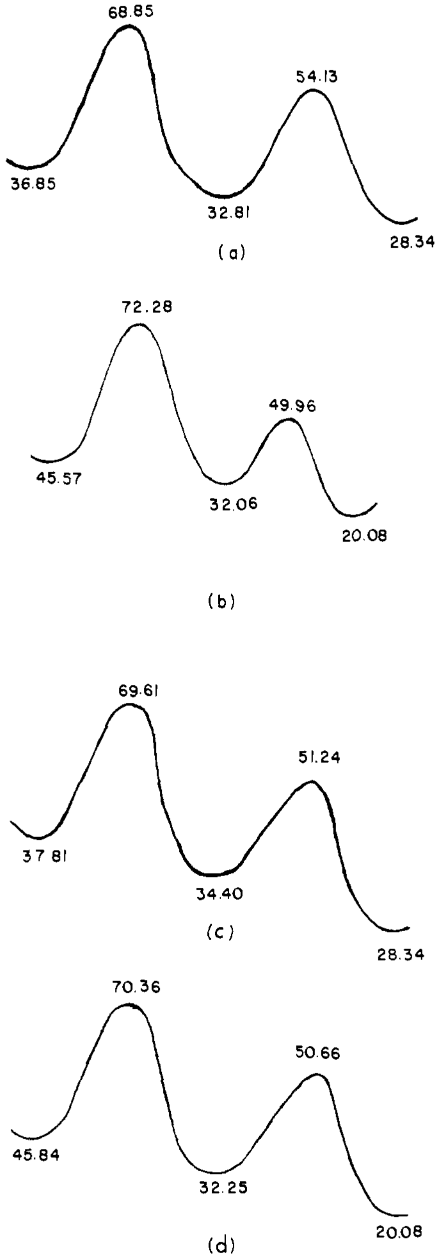

Figure 5. Reaction profiles for the thermolysis of **10** and **10**, calculated (a, c) by MNDO; (b, D) by MINDO/3.

D. 1,4-Cyclohexadien-2,5-ylene-1,1-diazene (14). The last reaction studied was the reverse cheletropic loss of nitrogen (**15**) from 1,4-cyclohexadien-2,5-ylene-1,1-diazene (**14**) to form benzene (**8**), a process isoelectronic with the loss of carbon monoxide (**3**) from **7**. Figure 7 shows the geometry and other properties calculated for **14** by MINDO/3 and MNDO. Since the conversion of **14** to (**8** + **15**) is extremely fast, no experimental data for **14** are available for comparison. The geometries predicted by both procedures are similar but the MINDO/3 heat of formation is less positive than the MNDO one by 29.5 kcal/mol. The heats

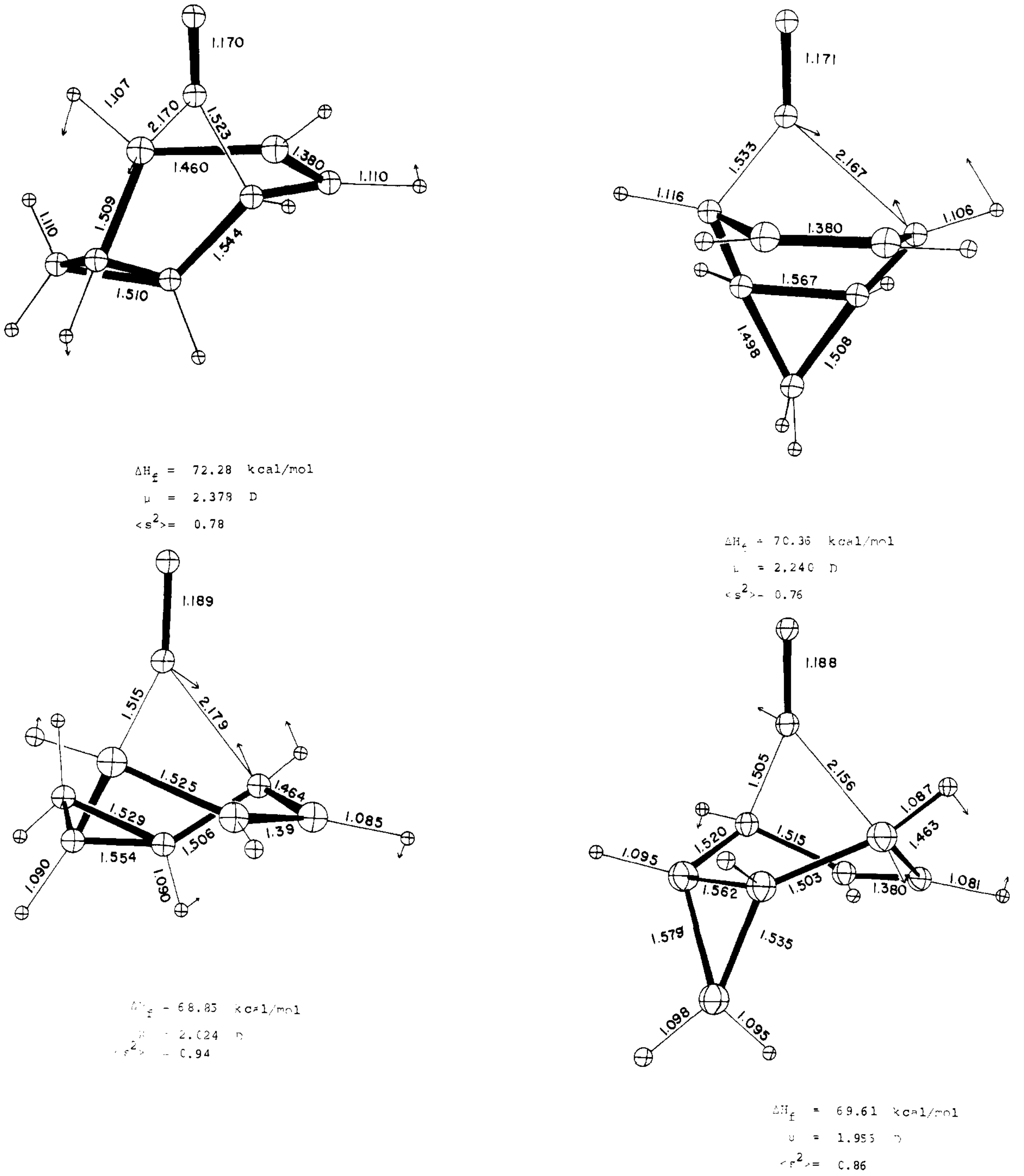

Figure 6. Geometries and other properties calculated for the transition states for thermolysis of (a, b) **10**; (c, d) **11**. (a, c) MINDO/3; (b, d) MNDO.

of reaction calculated for the overall conversion of **14** to (**8** + **15**) differ correspondingly:

$$\Delta H\text{: MINDO/3, } -63\text{ , MNDO, } -99.3\text{ kcal/mol} \qquad (2)$$

Similar differences were observed in our previous studies[2] of the thermolyses of cyclic diazenes. For reasons indicated there, the MNDO heats of formation and reaction are expected to be nearer to the truth. The thermolysis of **14** is in any case predicted to be extremely exothermic, as would be expected in view of the exothermicity of similar reactions of simpler diazenes and the fact that the product (**8**) here is aromatic.

The results given by our studies of the reaction, using MINDO/3 and MNDO, are illustrated by the reaction profiles shown in Figure 8. In contrast to the isoelectronic decarbonylation of 7, the conversion of **14** to (**8** + **15**) was predicted by both methods to take place in a concerted manner, as indicated by the reaction profiles in Figure 8. Furthermore, both procedures led to very low activation energies for the reaction (MINDO/3, 4.0; MNDO, 2.8 kcal/mol), showing that biradical-like intermediates are not involved. Moreover, recalculation of the energies of the TS, using UMINDO/3 or UMNDO, led to energies almost identical with the RHF procedures.

All attempts to prepare **14** have so far led only to its decomposition products, **8** and **15**, implying that decomposition of **14** is, as predicted, as extremely fast process.

Our earlier calculations[2] for the decompositions of simple cyclic diazenes predicted them to take place nonsynchronously, via very unsymmetrical TS leading to biradical-like intermediates. In the case of **14**, however, MNDO predicted the TS to be symmetric, the lengths of the breaking C–C bonds being equal. While the MINDO/3 TS was not symmetrical, the breaking bonds in it, while unequal in length, are both much longer (1.596, 1.867 Å) than in **14** itself (1.568 Å). Thus both procedures agree in pre-

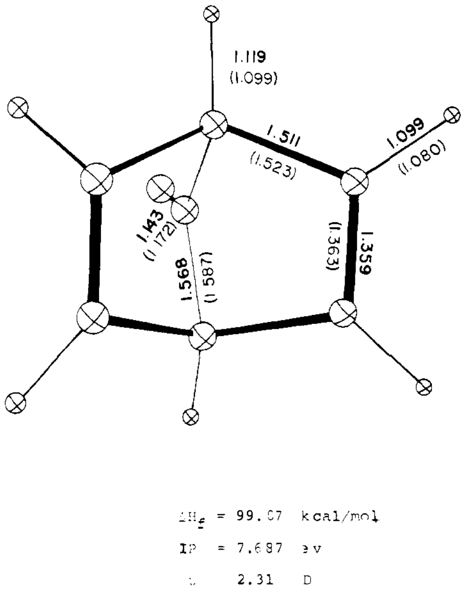

Figure 7. Geometries and other properties calculated for **14** by MINDO/33 (MNDO).

dicting the decomposition of **14** to take place in a much more nearly synchronous manner than the other reactions discussed in here and the preceding paper.

E. Mechanisms of Cheletropic Reactions. The results reported here imply that all but one of the reactions studied take place in a manner similar to the reverse cheletropic reactions of monocyclic ketones and diazenes, i.e., by a nonsynchronous mechanism involving a very unsymmetrical TS in which one of the breaking bonds is still almost intact. Evidently there is some factor inhibiting synchronicity, at least so far as the calculations reported here, and in the previous paper,[2] are concerned. The one exception, i.e., the thermolysis of **14**, is in effect one which proves the rule because the activation energies of the synchronous (MNDO) or almost synchronous (MINDO/3) paths are so very low. They are low because of the extreme exothermicity of the reaction, due in turn in no small part to the fact that it leads to an aromatic product. A nonsynchronous path of the kind followed by the other reactions considered here would lose this advantage. Since the "unfavorable" synchronous path is so very facile, nothing is then gained by following a two-step[8] or two-stage[8] route. Similar situations arise in the case of certain reactions that are "forbidden" by the Woodward–Hoffman rules[14] or Evans' principle.[15] Thus the "forbidden" electrocyclic conersion of bicyclopentene (**16**) to 1,3-cyclopentadiene (**17**) undoubtedly takes place synchronously.[16] Here the activation energy for the "forbidden" synchronous path is small because of the relief of extensive ring strain during the reaction. Equally, nonsynchronous paths involving biradical intermediates are unfavorable because the corresponding unsymmetrical TS would be more highly strained than the symmetrical one involved in the synchronous route.

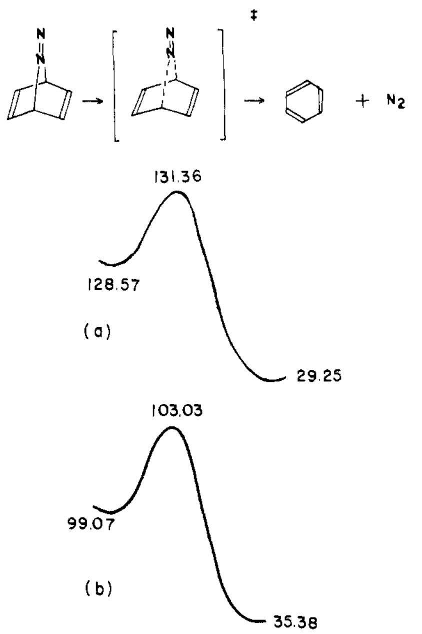

Figure 8. Reaction profiles for the thermolysis of **14** calculated (a) by MNDO; (b) by MINDO/3.

As pointed out in the preceding paper,[2] cheletropic reactions can be regarded as a special kind of cycloaddition, and previous studies[12] have indicated that conventional cycloadditions (e.g., Diels–Alder reactions) also take place in a nonsynchronous manner via very unsymmetrical transition states. These conclusions naturally rest on the assumption that MINDO/3 and MNDO do not suffer from a predisposition against synchronous mechanisms. Reasons for believing this to be so have already been presented,[2] and a fuller account is given in a paper discussing the mechanisms of two-bond[17] reactions in general.

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Communications to the Editor

Enhanced Sodium Cation Binding by Electrochemically Reduced Nitrobenzene-Substituted Lariat Ethers

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An important advantage of lariat ethers[1] over monocyclic crown ethers is the presence of a side arm whose properties may be varied to control binding and, it is hoped, selectivity. Moreover, the potential exists for reversibly switching the ligand and altering its binding strength on demand. Photoswitching,[2] ionization of acidic functions,[3] protonation of amines,[4] and oxidative dimerization of sulfhydryl-substituted crowns[5] have all been utilized to one degree or another as reversible switching mechanisms. We report here the first evidence for electrochemically controlled electron-transfer switching and intramolecular ion-pair formation in nitrobenzene-derived lariat ethers.

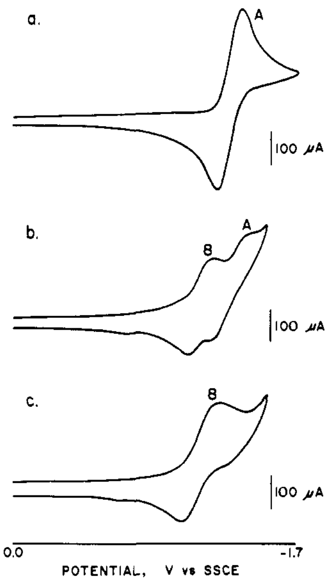
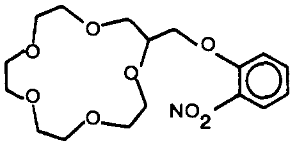


Figure 1. Cyclic voltammograms for 2-(2-nitrophenoxy)methyl-15-crown-5 (**1**) in the (a) absence and (b) presence of 0.5 equiv and (c) presence of 1 equiv of $Na^+ClO_4^-$.

2-(2-Nitrophenoxy)methyl-15-crown-5 (**1**) was prepared by treating the anion (NaH, THF) of 2-hydroxymethyl-15-crown-5[6] with 1 equiv of 1-chloro-2-nitrobenzene (25 °C, 4 h). The crown was a pale yellow oil isolated (55%) by chromatography over alumina.[7] 2-(4-Nitrophenoxy)methyl-15-crown-5 (**3**) was prepared analogously and isolated (bp 175 °C (0.1 mm)) as a yellow oil in 74% yield.[7] All electrochemical experiments were conducted under dry N_2 in MeCN 0.1 M in Bu_4NClO_4. A standard three-compartment cell, glassy carbon (0.35-cm² surface), and Pt wire electrodes were used. $E^{\circ\prime}$ values are reported vs. an aqueous Na^+-saturated calomel electrode (SSCE). Measurements



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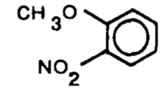

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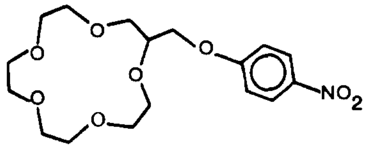

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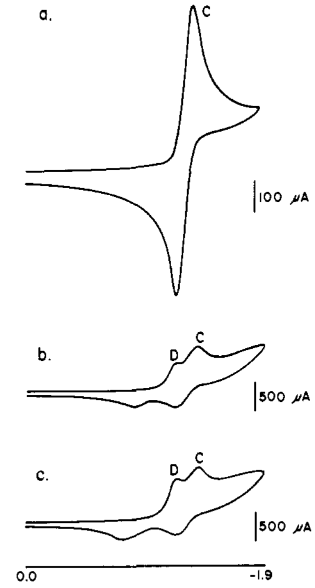

Figure 2. Cyclic voltammograms for 2-nitroanisole (**2**) in the (a) absence and (b) presence of 0.5 equiv and (c) presence of 1.0 equiv of $Na^+ClO_4^-$.

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(7) (a) Compound **1**: ^1H NMR ($CDCl_3$, ppm) 3.9 (m, 21 H), 6.9–8.1 (m 4 H). Anal. Calcd for $C_{17}H_{25}NO_8$: C, 54.98; H, 6.78; N, 3.77. Found: C, 54.62; H, 6.91, N, 3.78. (b) Compound **3**: ^1H NMR ($CDCl_3$, ppm) 3.7 (m, 21 H), 7.0–8.2 (dd, 4 H). Anal. (Isomer of **1**) found: C, 54.99; H, 6.95; H, 3.90.

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