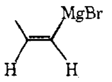
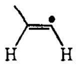
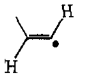
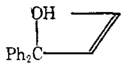
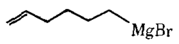
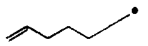
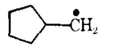
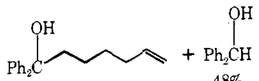
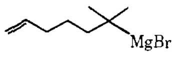
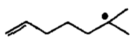
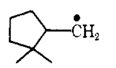
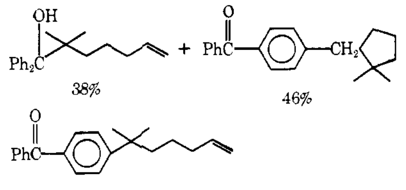
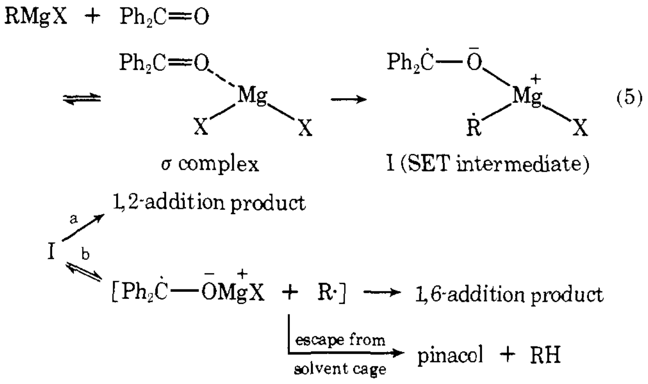
Table I. Grignard Reagent Radical Probe Results

Grignard reagent	Expected intermediate	Isomerized or cyclized radical	Product of intermediate with benzophenone
			 100%
			 52% + 48%
			 38% + 46%; 16%



the ketyl ($R_2\dot{C}—O^-$) which in turn would determine the amount of SET character observed in the reaction. With tertiary Grignard reagents, the intermediate complex would be unstable owing to the stability of the *tert*-alkyl radical, thus making path b competitive with path a or even the predominant reaction pathway. On the other hand, vinylic Grignards (*cis*-C_3H_5MgBr) and primary alkyl Grignards ($C_6H_{11}MgBr$) may react by a polar mechanism or if, by SET, form a more stable complex which would collapse via path a to give only 1,2-addition product with no SET character observed (as in the cases reported here).

The possibility that polar and SET mechanisms are competitive, depending principally on the reduction potential of the ketone and the oxidation potential of the Grignard reagents, seems quite clear. At the two ends of the spectrum, all evidence indicates that the reaction of *t*-C_4H_9MgCl with benzophenone is SET in nature, whereas the reaction of CH_3MgBr with acetone is polar in nature. Since no isomerization of the *cis*-C_3H_5MgBr or cyclization of the $C_6H_{11}MgBr$ probes were observed it is not clear whether these reactions proceed by a polar or SET pathway (or both). However, it is clear from this work that, if these reactions proceed by a SET pathway, a "free radical" is not involved. It is also clear that the mechanism initially proposed by Blomberg-Mosher[8] and Fauvarque[9] and later supported by Holm-Crossland[1] for the reaction of *t*-C_4H_9MgCl with benzophenone needs some modification. A "free radical" and "free ketyl" cannot form in the SET step as was proposed. Apparently an intermediate radical anion-radical cation pair is formed which can collapse to give 1,2-addition product or dissociate to form a radical anion and a free radical within the solvent cage which in turn can collapse to conjugate addition products or escape the solvent cage to form pinacol.

References and Notes

(1) The authors gratefully acknowledge the support of the National Science Foundation Grant No. MPS-7504127.
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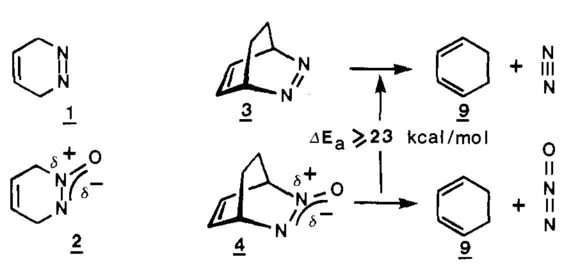
Energetics of Heteroextrusion Reactions. N_2 vs. N_2O[1]

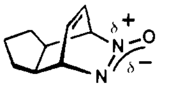
Sir:

1,2-Diazacyclohexa-1,4-dienes **1** are known as exceptionally labile intermediates expelling nitrogen at −78 °C with a half-life of 30 s or less.[2,3] *N*-Oxides **2**, on the other hand, are shelf-stable substances which lose N_2O at a comparable rate some 300 °C higher. Although it has been established that fragmentation of both the cyclic unsaturated azo system[3] and the corresponding azo *N*-oxide[1,4] is concerted, the origin of the great difference between the two energy barriers has remained obscure. The gap amounts to $\Delta E_a = E_a(\text{azoxy}) - E_a(\text{azo}) \geq 23$ kcal/mol, and, assuming that $\Delta E_a = \Delta\Delta G^*$, $k_{\text{azo}}/k_{\text{azoxy}} \geq 10^{17}$ at 25 °C.[4,5]



In the present contribution we report thermochemical data for the azo *N*-oxide retrocycloaddition which permits the relative azo/azoxy hypersurfaces to be compared quantitatively. New light is shed on the origin of the large difference between the activation barriers for the two heteroextrusion reactions. In addition an estimate of the heat of formation for the *cis*-azoxy moiety is made.

Heats of reaction for the thermal elimination of N_2O from the azo *N*-oxides **4**, **5**, **6**, **7**, and **8** have been determined by temperature programmed calorimetry (DSC).[7] Compounds



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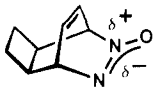

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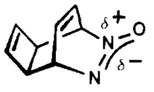

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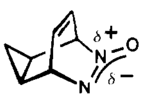

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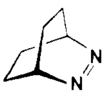
6, **7**, and **8** gave thermograms that could be perfectly fitted with theoretical first-order curves. Compounds **4** and **5**[8] gave thermograms of more complex shape since the unsaturated products formed, namely 1,3-cyclohexadiene (**9**) and bicyclo[4.3.0]nona-2,4-diene, take part in secondary reactions occurring at the thermolysis temperature.[9] Deconvolution of the thermograms however, permits the determination of the enthalpies of the cycloreversion of these compounds as well. The results of the measurements are listed in Table I.

To compare reactivities of species **1** and **2**, the heat of the reaction for the extrusion of molecular nitrogen from a *cis*-azoalkane of type **1** is required. Although this value has not been experimentally determined owing to the lability of the latter, it can be estimated for azo **3** from the $\Delta H°_f$ of 2,3-diazabicyclo[2.2.2]oct-2-ene (**10**) corrected for the introduction of a double bond.[10] The value for **10**, 38.5 kcal/mol, is derived from the measured $\Delta H°_f$ of the dimethyl derivative **11**[11] and Benson and coworker's thermochemical tables.[12] Bicyclic unsaturation and the associated strain is accounted for by considering the energy difference between bicyclo[2.2.2]oct-2-ene (**12**) and bicyclo[2.2.2]octa-2,4-diene (**13**) as obtained from force field calculations (31.8 kcal/mol).[13]



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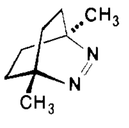

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$$\Delta H°_f\,(\mathbf{3}, \text{g}, 298\ \text{K}) = \Delta H°_f\,(\mathbf{10}) - \Delta H°_f\,(\mathbf{12}) + \Delta H°_f\,(\mathbf{13})$$
$$= 38.5 - 7.9 + 39.7 = 70.3\ \text{kcal/mol}$$

The heat of reaction for N_2 release from bicycle **3** in the gas phase (298 K) is consequently evaluated as −44.9 kcal/mol. The derived value is in good agreement with a calculation of ΔH_r for the concerted retrocycloaddition of a cyclopropane substituted azoalkane (−45.7 kcal/mol).[14] The energy profile for deazetation (Figure 1) can be constructed since we also know that $\Delta G^* (\mathbf{3} \rightarrow \mathbf{9} + N_2) = \Delta H^* (\mathbf{3} \rightarrow \mathbf{9} + N_2) \leq 14$ kcal/mol.[1,2b,4]

$$\Delta H_r\,(\mathbf{3} \rightarrow \mathbf{9} + N_2, \text{g}, 298\ \text{K}) = \Delta H°_f\,(\mathbf{9}, \text{g}, 298\ \text{K})$$
$$- \Delta H°_f\,(\mathbf{3}, \text{g}, 298\ \text{K}) = 25.4 - 70.3 = -44.9\ \text{kcal/mol}$$

We can also establish on a common energy scale the profile for the related cycloregression of *N*-oxide **4**. The heat of this reaction as measured in solution is reported in Table I. Several corrections have to be considered in order to obtain the enthalpy of the reaction in the gas phase at 298 K: (i) the difference in the heat of solution of **4** and **9**; (ii) reduction of the reaction heat from 452 to 298 K; (iii) an adjustment of the pressure of gaseous N_2O in the sealed ampule (~20 atm) to standard conditions; and (iv) the difference in the heats of vaporization of **4** and **9**. Corrections i-iii are small (<2 kcal/mol)[15] in relation to the other thermal effects and therefore for the present purposes will be ignored. For iv we take ΔH_{vap} (**4**) = 20 ± 4 kcal/mol[17] and ΔH_{vap} (**9**) = 8 ± 1 kcal/mol[19] leading to the relation $\Delta H_{\text{vap}} = 8 - 20 = -12 \pm 5$ kcal/mol. Thus the corrected heat of reaction for the retrocycloaddition of azo *N*-oxide **4** is computed to be −13 kcal/mol. Comparison of this value with that found for the deazetation of **2** indicates that the loss of nitrogen is ~30 kcal/mol more favorable than the corresponding loss of N_2O.

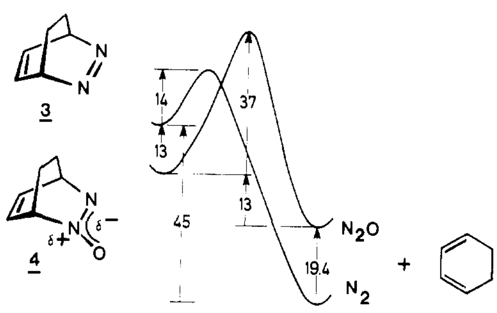

Figure 1. The energetics of the cycloreversion of azo **3** and azo *N*-oxide **4** (298 K, g), kcal/mol.

$$\Delta H_r\,(\mathbf{4} \rightarrow \mathbf{9} + N_2O, \text{g}, 298\ \text{K})$$
$$= -0.84 - 12 = -13 \pm 5\ \text{kcal/mol}$$

From an iterative fitting of the thermograms and from previous measurements,[1] we also know the activation enthalpy of the reaction to be 37 ± 2 kcal/mol. Since $\Delta H_f\,(N_2O, \text{g}, 298\ \text{K}) = 19.4$ kcal/mol, the full energy profile can be established.

Compilation of the various energy values from the thermochemical and kinetic measurements for N_2 and N_2O extrusion permits the construction of the energy profiles shown in Figure 1. Although this diagram can undoubtedly be refined by further thermochemical studies, we believe that it constitutes an accurate qualitative representation of the relative azo and azo *N*-oxide energetics. The relative position of the two transition states along the reaction coordinate is the result of applying Hammond's postulate[20] to the extrusion reactions.[21] If the postulate is applicable in the present situation, comparison of the two energy profiles suggests that the high exothermicity of the cycloreversion of **3** contributes to a depression of its enthalpy of activation and renders this reaction much more rapid that the cycloreversion of **4**.

One of the notable successes of the Woodward–Hoffmann precept has been the notion that "allowed" pericyclic reactions occur with a decisively lower energy requirement than the comparable "forbidden" transformation.[22] For similar overall reactions large energy differences are consequently often viewed as reflecting either forbidden or nonpericyclic pathways as compared with a genuine concerted one. When viewed via the elegant simplicity of the orbital symmetry conservation principle, heteropericyclic reactions are frequently enigmatic. Electrocyclic ring closure of heterosubstituted polyenes, for example, may diverge from expectations based on the corresponding symmetrical hydrocarbon.[23] Likewise many cycloadditions, formally forbidden under the constraints of various formulations of the orbital symmetry rules,[24] proceed with significantly reduced energy barriers under the influence of a strong unsymmetrical perturbation.[24b,25] The azo-azoxy decomposition rate ratio was originally interpreted[26] as an example of the reverse situation, a formally allowed, concerted reaction rendered more difficult by asymmetrization. The present work emphasizes that a large difference in reaction enthalpy for two closely related heterocyclic reactions may contribute to a large difference in activation energies and consequently in rates. Clearly mechanistic conclusions based on relative rates alone can be misleading.

As reported in Table I it has been possible to evaluate by DSC the heat of reaction for deazoxetation of four other azo

Table I. Heat of Reaction for Deazoxetation of Some Unsaturated Azo *N*-Oxides

Compd	No. of runs	T,[a] K	Solvent	$-\Delta H_{\text{react}}$,[b] kcal/mol
4	6	452	THF-d_8	0.84 ± 0.06
5	3	446	THF-d_8	0.71 ± 0.12
6	4	426	THF-d_8	2.31 ± 0.09
7	5	413	THF-d_8	9.85 ± 0.13
	5	422	CD_3CN	9.34 ± 0.23
8	4	337	THF-d_8	16.38 ± 0 85
	4	341	CD_3CN	14.99 ± 0.34

[a] Temperature at which the maximum heat flux due to the reactions is observed. [b] All errors are reported as ±2 $\bar{s}$; see J. D. Cox and G. Pilcher "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y. 1970, pp 43, 44.

N-oxides. By combination of these quantities with thermochemical group increments and reasonable strain energies, it is possible to arrive at an approximate heat of formation for the azo *N*-oxide group: $\Delta H°_f$ (*cis*-azo *N*-oxide) = 35–40 kcal/mol.[27] In view of the recently established $\Delta H°_f$ for the *cis*-azo group (54 kcal/mol),[14] oxidation of the azo to the azoxy moiety is clearly a highly exothermic process (15–20 kcal/mol).[28] The resulting thermochemical stabilization is in accord with the formation of a new σ bond, π-electron delocalization over the three heteroatoms, and the elimination of the azo α lone-pair repulsion.

Acknowledgments. We are grateful to the Danish Natural Science Research Council (jr. no. 911-5153) and to the "Fonds National Suisse pour le recherche scientifique" for their generous financial support and to Dr. Knud Andersen (H. C. Ørsted Institute, University of Copenhagen) for quantifying the value of correction iii.

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(5) ΔE_a and $k_{\text{azo}}/k_{\text{azoxy}}$ have been recalculated[4] assuming a $\Delta S^* = +5.0$ eu.[6]
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(8) Prepared by a route analogous to the other unsaturated azo *N*-oxides.[1,4] Compound **5** exhibits consistent spectroscopic properties and yields a satisfactory elemental analysis.
(9) For each run the sealed Pyrex ampules were monitored after thermolysis by ^{13}C and ^1H NMR. With the exception of **4** and **5** the only observable product was the diene corresponding to retrocycloaddition. For the former, in addition to the primary products, benzene (for **4**) and dimers (for **4** and **5**) were detected.
(10) We are grateful to P. Engel (Rice University) for suggesting this method for arriving at $\Delta H°_f$ (**3**).
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(15) The diminutive value of correction i is substantiated by the data in Table I. Factor ii is small since, although $C_p{}^0$ (gas) values for individual species may be large, $\Delta C_p{}^0$ (gas) for reactions is considerably less and consequently responds insignificantly to changes in temperature (cf. ref 13a, pp 20, 32). We calculate 0.5–1.7 kcal/mol. With regard to correction iii, it should be pointed out that N_2O is most likely in the gas phase during the calorimetric measurements since its critical temperature is T_c 36.5 °C and its critical pressure is $P_c = 74.1$ atm. Assuming nonideal gas behavior, application of either the principle of corresponding states [16a] or the virial equation with maintenance of the second virial coefficient[16b] leads to a pressure correction of 0.08 kcal/mol.
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(17) The heat of vaporization of 2,3-diazabicyclo[2.2.1]hept-2-ene and 2,3-diaza-1,4-dimethylbicyclol[2.2.2]oct-2-ene have been determined to be 13.2 and 17.2 kcal/mol, respectively.[11] The difference in dipole moment between 2,3-diazabicyclo[2.2.2]oct-2-ene and the corresponding *N*-oxide is 1.6 D.[18] Consequently a ΔH_v (**4**) = 20 ± 4 kcal/mol is assumed.
(18) Dr. C. Larsen, University of Copenhagen, unpublished results.
(19) Estimated to be 8.3 kcal/mol by the method of Wadsö: I. Wadsö, *Acta Chem. Scand.*, **20**, 544 (1966).
(20) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
(21) Ordinarily this principle is safely utilized, if the energy of the potential minimum in question is "nearly the same" as that of the corresponding transition state (cf. D. Farcasiu, *J. Chem. Educ.*, **52**, 76 (1975)). For *N*-oxide **4** the resemblance between starting material and transition state would not seem to be overwhelming.
(22) Various limits for *E* ("forbidden"–"allowed") have been suggested (10–20 kcal/mol): ref 2b; K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Am. Chem. Soc.*, **94**, 5639 (1972); J. I. Brauman and W. G. Archie, Jr., *ibid.*, **94**, 4262 (1972); P. Merlet, S. D. Peyerimhoff, R. J. Buenker, and S. Shih, *ibid.*, **96**, 6810 (1974); W. L. Mock, *ibid.*, **97**, 3666 (1975); and references found in these papers.
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(27) In accord with the procedure indicated for the calculation of $\Delta H°_f$ (**3**, g, 298 K), the quantities ΔH_r (298 K, g, Table I), $\Delta H°_f$ (cyclic dienes) and $\Delta H°_f$ (N_2O) were combined to give an average value for $\Delta H°_f$ (*cis*-azo *N*-oxide).
(28) Although the oxidation of amines and pyridines to the corresponding *N*-oxides is generally acknowledged to be an exothermic process, to our knowledge this is the first quantitative estimate of the energy gain.

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Generation and Capture of Common Intermediates from Proto-Planar and Proto-Bisected Trimethylenemethane Precursors. Thermal Rearrangement of a Methylenepyrazoline[1]

Sir:

Theory suggests[2] that the stable forms of triplet and singlet trimethylenemethanes (TMMs) should be, respectively, planar and bisected. We now report the results of an attempt to generate a planar and a bisected TMM independently by decomposition of the isomeric methylenepyrazolines **1** and **2.** The "proto-planar" bridged compound **1** could be imagined to lose molecular nitrogen thermally and give a planar singlet without any torsion about the bond joining the exocyclic Me_2C group to the five-membered ring, whereas the "proto-bisected" fused compound **2,** by a similar process and rehybridization of that group, would give a bisected TMM. If these TMM species have separate existences as long as 10^{-9} s, it might be possible to capture them with external reagents and observe different products from each.

For such a study to be interpretable, it is necessary to show that the methylenepyrazolines **1** and **2** have separable pathways of deazetation. Without this information, common