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Structure and Reactivity in the Reduction of Cycloalkenes and Cycloalkadienes by Diimide[1]

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The reduction of alkenes by diimide is believed to consist of a single step in which the diimide, formed in situ, transfers a pair of hydrogen atoms to the olefinic center by a synchronous suprafacial process via a transition state of negligible ionic character.[2–5] The relative rates of diimide reductions of nearly 40 cyclic, exocyclic, and acyclic alkenes have been determined by Garbisch, Schildcrout, Patterson, and Sprecher.[6] They concluded that the major factors that contribute to the differences in reactivity are torsional strain, bond angle bending strain, and the α-alkyl substituent effect and, in support, cited the good agreement between the calculated and observed values for the relative rates. Bird, Franzus, and Surridge[7] concluded that the relative rate of reduction of the nonconjugated dienes (nonbornadienes) is a function of the degree of substitution of the double bond attacked. In our previous paper[8] we proposed that Garbisch's general approach (for estimating the contribution of torsional strain and bond angle strain to the relative reactivities of alkenes) can be extended to conjugated dienes by an appropriate estimate of the conjugation energy which diminishes as the geometry of the conjugated system departs from planarity.[8,9]

To provide additional information on the effect of ring size upon the reactivity of cycloalkadienes, we have determined the relative rate constants for the sequential reduction of some conjugated and nonconjugated cycloalkadienes to the derived cycloalkenes and cycloalkanes, and through a series of competitive reactions, the relative rates of reduction of cycloalkenes and cycloalkadienes of different ring size ($C_5 \rightarrow C_{12}$). The reductions were carried out at 25 °C with diimide which was generated from the decomposition of azodicarboxylic acid produced by the slow addition of a methanol solution of acetic acid to potassium azodicarboxylate in methanol.[7,8]

Results and Discussion

The competitive reductions of cycloalkenes by diimide generated from the decarboxylation of azodicarboxylic acid at 25 °C yielded relative rate constants whose values are compared in Table I to those calculated and found experimentally by Garbisch et al.[6] Each constant represents the average obtained from six to ten samples of the reaction mixtures which were removed at arbitrary intervals of time in each experiment. Some cross checks were done to verify the relative rates obtained indirectly. Since our experiments were done at 25 °C, rather than 80 °C, the relative rates were found to be larger than those reported by Garbisch et al.[6] but the general trend in the observed relative reactivities of the alkenes is in good agreement. Cyclopentene, cycloheptene, and *cis*-cyclooctene are considerably more reactive than cyclohexene and, according to Garbisch et al., *cis*-cyclononene and *cis*-cyclododecene are only slightly more reactive.[6] Bicyclo[2.2.1]heptene and *trans*-cyclooctene are by far the most reactive of the alkenes, a fact that is attributed to the unusually large bond angle bending and torsional strains (estimated to be 23.6 and 17.8 kcal/mole, respectively),[10] which are relieved in part upon reaching the transition state. The highly strained *trans*-cyclooctene is 22 000 times more reactive than cyclohexene at 25 °C.

For the 12-member ring, the cis isomer, which possesses a very low strain energy,[6] was found to react 1.4 times as fast as cyclohexene while Garbisch reports a relative rate of 0.6 (calculated 1.5).[6] However, the trans isomer was found to react eight times as fast, a fact attributed again to the relief of torsional strain as well as to the absence of the vicinal methylene–methylene interactions which are present in the cis isomer.

With respect to ring size, the trend found for the cycloalkadienes, however, was opposite to that of the cycloalkenes (Table II). The most reactive compound was 1,3-cyclohexadiene while cyclopentadiene, 1,3-cycloheptadiene, and 1,3-cyclooctadiene were reduced more slowly. Indeed the conjugated 1,3-cyclohexadiene was reported by Siegel, Forman, Fisher, and Johnson[8] to be more reactive than the corresponding nonconjugated diene as well as cyclohexene, when the rates are adjusted for the reactivity per double bond. They suggested that the expected rate-diminishing effect of conjugation in this instance is small because of the nonplanarity of the conjugated system which is due to internal torsional and bond angle strains.[8,9] The lower reactivity of other cyclic dienes relative to 1,3-cyclohexadiene arises because the decreased torsional strains in those dienes not only permits a more effective conjugative interaction in the diene (rate diminishing) but also results in a smaller driving force from the release of torsional strain at the transition state.

Ring size (Table II) influences the relative reactivity toward diimide of nonconjugated dienes in a manner which indicates the importance of the release of torsional strain as a driving force. Thus 1,5-cyclooctadiene, which has been estimated to have a torsional strain energy of 13.3 kcal/mol,[10] was found to react five times as fast as 1,3-cyclooctadiene while the unconjugated 1,4-cyclohexadiene, whose torsional strain appears to be relatively small,[9] has a lower reactivity than the corresponding conjugated diene, 1,3-cyclohexadiene.

The determination of the relative reactivity of a particular cyclic diene and the resulting monoene was obtained directly as before (Table III).[8] While for 1,3- and 1,4-cyclohexadiene, the reactivity (per double bond) of the diene is greater or equal to that of the monoene, the other cycloalkadienes examined are less restrictive per double bond than the corresponding monoene. This fact suggests again that although conjugation is important in tending to lower the reactivity of the alkenyl double bond, torsional strain (as in 1,3-cyclohexadiene) may

Table I. Summary of Relative Rates (Cross Checks) in the Reduction of Cycloalkenes with Diimide at 25 °C[a]

Registry no. (A)	Alkene A	Alkene B	k_A/k_B[b] (direct)	k_A/k_6[b]	k_a/k_6[c] (Garbisch et al.) 80 °C
142-29-0	c-C_5	c-C_6[f]	22 ± 1.5	22 ± 1.5	15.5
628-92-2	c-C_7	c-C_6	18 ± 1.0	18 ± 1.0	12.1
931-87-3	c-C_8 (cis)	c-C_7	1.69 ± 0.2	30.4 ± 0.9[d]	17.0
931-89-5	c-C_8 (trans)	c-C_7	1200 ± 80	$2.2 \times 10^3 \pm 500$[d]	
	c-C_8 (cis)	c-C_6	30.5 ± 1.0	30.5 ± 1.0	17.0
	c-C_8 (trans)	c-C_8 (cis)	740 ± 30	$2.2 \times 10^3 \pm 500$[d]	
1129-89-1	c-C_{12} (cis)	c-C_8 (cis)	0.05 ± 0.01	1.46 ± 0.3	0.64[e]
1468-75-5	c-C_{12} (trans)	c-C_8 (cis)	0.26 ± 0.12	8.0 ± 0.5	
279-23-2	Bicyclo[2.2.1]-C_7	c-C_6	690 ± 20	690 ± 20	
	Bicyclo[2.2.1]-C_7	c-C_7	36 ± 3	648 ± 40[d]	4.5×10^2
	Bicyclo[2.2.1]-C_7	c-C_8 (cis)	24 ± 2	732 ± 50	4.5×10^2
1192-37-6	Methylenecyclohexane	Methylenecyclopentane[g]	1.8 ± 0.3		3.5

[a] Diimide generated from decomposition of azodicarboxylic acid at 25 °C. [b] k_6 is for cyclohexene. [c] See ref 6. [d] Calculated from $k_A/k_6 = (k_A/k_B)(k_B/k_6)$. [e] Calculated value according to Garbisch et al. should be 1.5 (ref 6). [f] Registry no., 110-83-8. [g] Registry no., 1528-30-9.

Table II. Relative Rates for Competitive Reduction of Cyclic Dienes to Monoenes with Diimide Generated at 25 °C[a]

Registry no. A	Registry no. B	Dienes A	Dienes B	k_A/k_B (direct)	k_{6D}/k_A[b,c] (indirect)
592-57-4	542-92-7	1,3-Cyclohexadiene	Cyclopentadiene	2.0 ± 0.15	(1.00)
	628-41-1	1,3-Cyclohexadiene	1,4-Cyclohexadiene	22 ± 2.0 25.0[d]	
		1,3-Cyclohexadiene	1,3-Cycloheptadiene	9.0 ± 1.0	
	1700-10-3	1,3-Cyclohexadiene	1,3-Cyclooctadiene	27 ± 2	
4054-38-0		1,3-Cycloheptadiene	1,3-Cyclooctadiene	3.2 ± 0.6	8.6
111-78-4		1,5-Cyclooctadiene	1,3-Cyclooctadiene	5.5 ± 1.0	5.0
		1,3-Cyclohexadiene	1,5-Cyclooctadiene	5.0 ± 0.5	

[a] Diimide generated from decomposition of azodicarboxylic acid at 25 °C. [b] k_{6D} is for 1,3-cyclohexadiene reduced to cyclohexene. [c] Calculated from $k_A/k_{6D} = (k_A/k_B)(k_B/k_{6D})$. [d] From ref 8.

Table III. Relative Reactivities of Cycloalkadienes and Product Monoenes in the Reduction of Diimide at 25 °C[a]

$$\text{diene} \xrightarrow{k_1} \text{monoene} \xrightarrow{k_2} \text{saturated}$$

Diene	Monoene	k_2/k_1[b]
c-C_5-diene	Cyclopentene	1.75 ± 0.3
1,3-c-C_6-diene	Cyclohexene	0.04[c]
1,4-c-C_6-diene	Cyclohexene	0.45 ± 0.1
1,3-c-C_7-diene	Cycloheptene	6.5 ± 0.9
1,3-c-C_8-diene	*cis*-cyclooctene	35 ± 4.0

[a] Diimide generated from the decomposition of azodicarboxylic acid. [b] *Per double bond,* the relative reactivities are 3.5, 0.08, 0.9, 13, and 70 (in descending order in the table). [c] Value obtained from ref 8.

reduce the planarity of the conjugated system and thus the conjugative interaction as well.

Experimental Section

Dienes and Alkenes. The cycloalkenes and cycloalkadienes were purchased from Chemical Samples Co. or Aldrich Co. and used without further purification except for 1,5-cyclooctadiene and *cis*- and *trans*-cyclododecene, which were obtained from Columbian Carbon Co. and were redistilled before use. The identity of each compound was checked by examining its NMR and infrared spectra and its purity was at least 99% as determined by GLC.

Reduction with Diimide. Competitive reductions with diimide generated from the decarboxylation of azodicarboxylic acid in methanol at 25 °C followed the procedure of Bird et al.[7] with relatively minor modifications.[8]

Analytical Procedure. The mixtures were analyzed by GLC (flame ionization detector) on either a 45 ft × 0.125 in. column of 2.5% Carbowax 600 and 2.5% Carbowax 750 on Chromosorb W (AW) 60/80 mesh (for the cyclic dienes and products) or a 300 ft × 0.02 in. capillary column coated with 10% Apiezon L. All peaks were identified by comparison with mixtures of authentic standards and the molar response factor of each component was determined. The peak areas were obtained with a digital integrator, Varian Model 485. The calculations of the relative rate constants from competitive reductions or the consecutive reactions of a diene were obtained by the equations and methods described in our previous paper.[8]

Registry No.—Diimide, 3618-05-1.

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