ductions ever achieved with optically active 1,4-dihydropyridines.[6] The consistent formation of an excess of the *S* enantiomer (the relative priorities of the groups are the same for all the optically active alcohols allowing direct comparison) strongly suggests structurally related transition states for reduction. ^{1}H NMR shielding effects in the presence of Mg^{2+} indicate complexation of Mg^{2+} close to the diethylene glycol bridge of **6**. Assuming that the oxygen of carbonyl group complexes to Mg^{2+} with the carbonyl carbon oriented toward the 4 position of the 1,4-dihydropyridine, that the phenyl substituent is the largest group, and that complexed α-dicarbonyl compounds assume a cis conformation for the carbonyl groups, the observed *S* configurations can be predicted. It is important to note that **6** is rather rigid owing to the two amide linkages.

Further experiments are in progress.[19]

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J. G. de Vries, Richard M. Kellogg*

Department of Organic Chemistry, University of Groningen Nijenborgh, 9747 AG Groningen, The Netherlands

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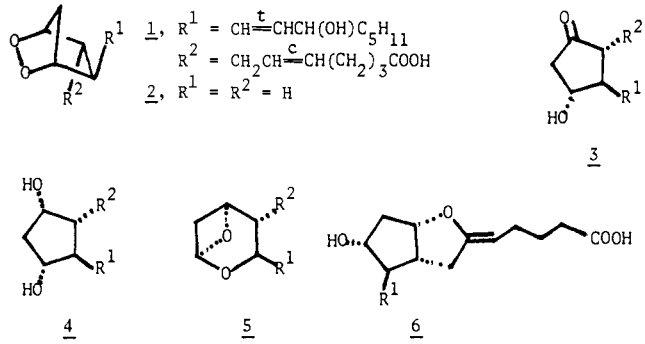
Extraordinary Reactivity of the Prostaglandin Endoperoxide Nucleus. Nonpolar Rearrangement of 2,3-Dioxabicyclo[2.2.1]heptane and -[2.2.2]octane

Sir:

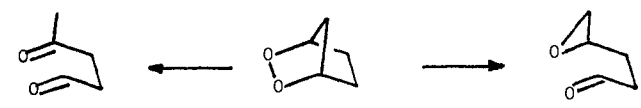
Occasionally Nature provides us with molecules which not only have unusual structures, but which also exhibit extraordinary chemical reactivity. Prostaglandin (PG) endoperoxides[1] (e.g., **1**) possess an unusual bicyclic peroxide nucleus **2**.[2] They are a branch point in the oxidative transformation of polyunsaturated fatty acids into a vast array of physiologically active metabolites.[3] The biological role of **1** depends in large measure on enzymatic conversion into prostaglandins (e.g., **3**, **4**), thromboxane A_2 (**5**),[4] and prostacyclin (**6**).[5] To provide a basis



3 4 5 6

for interpreting the complex biochemistry of **1**, we are studying the chemistry of the model endoperoxide **2** and homologues. We now report that the abnormally large solvent effects found for thermal decompositions of **2**[6] are not observed for decomposition of the less strained homologue, 2,3-dioxabicyclo[2.2.2]octane (**7**).[7] Furthermore, activation enthalpies and entropies for thermal decomposition of **2**, of the homologue **7**, and of *tert*-butyl peroxide in cyclohexane are remarkably different. $\Delta H^{\ddagger}$ increases with decreasing strain in the series.

Thermal decompositions of **2** and **7**[7] were monitored by ^{1}H NMR. Relative rates in various solvents are listed in Table I. Both reactions follow first-order kinetics. As reported previously, the rate of decomposition of **2** increases with solvent polarity and is exceptionally rapid in protic solvents owing primarily to an extraordinary dependence of the rate of rearrangement to levulinaldehyde (**8**) on solvent polarity.[6] The parallel first-order rearrangement of **2** to **9** is a nonpolar process which shows only a small dependence on solvent polarity.



8 2 9

In contrast, the rate of decomposition of **7** varies only slightly and erratically with changes in solvent polarity. The modest acceleration found for decomposition of **7** in protic solvents

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Table I. Solvent Effects for Decomposition of Peroxides **2** and **7**

reaction solvent	dielectric constant[a]	rel rates 7 (at 130 °C)	rel rates 2 (at 73 °C)
cyclohexane-d_{12}	1.94	1.0[b]	1.0[c]
benzene-d_6	2.18	0.8	1.4
chlorobenzene	4.85	1.1	2.4
CD_3COOD	6.63	2.7	26.0
$ClCD_2CD_2Cl$	7.94	1.5	2.7
2-butanone	14.35	1.3	2.8
CD_3CN	28	1.8	4.4
H_2O	73 (at 40 °C)	6.2	*d*

[a] Estimated for 73 °C. [b] $k = 5.2 \times 10^{-5}$ s^{-1}. [c] $k = 4.4 \times 10^{-5}$ s^{-1}. [d] $k = 160 \times 10^{-5}$ (at 40 °C).

Table II. Solvent Effects on Yields of Ethylene from Decomposition of **7**

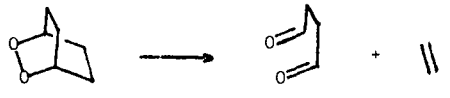
reaction solvent	ethylene yield, %	reaction solvent	ethylene yield, %
cyclohexane-d_{12}	23	CD_2ClCD_2Cl	37
benzene-d_6	37	CD_3CN	100
chlorobenzene	31		

Table III. Rate Constants for Thermal Decomposition of **2** and **7** in Cyclohexane-d_{12}[12]

peroxide	reaction temp, °C	$k \times 10^5$, s^{-1}
2	57.0	0.95 ± 0.15
2	60.0	1.57 ± 0.14
2	65.0	2.69 ± 0.11
2	73.0	4.44 ± 0.27
2	76.0	6.55 ± 0.31
7	120.0	2.03 ± 0.15
7	130.0	5.24 ± 0.21
7	131.0	5.56 ± 0.21
7	135.0	8.85 ± 0.57
7	140.0	13.46 ± 1.8
7	145.0	25.06 ± 1.0
7	150.0	44.02 ± 1.3

contrasts with the uniquely profound effect observed for **2**.[6] Thus, even the close analogue **7** does not possess the unusual reactivity of the biologically important bicyclic peroxide **2**.

Both succinaldehyde (**10**) and ethylene were produced in decomposition of **7**. However, **10** is not stable under the reac-

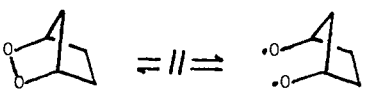


7 **10**

tion conditions. Yields of ethylene, determined by GLC after conversion into 1,2-dibromoethane, are listed in Table II for various reaction solvents. The quantitative yield of ethylene in acetonitrile is consistent with the ability of this solvent to promote β scission of alkoxy radicals.[8]

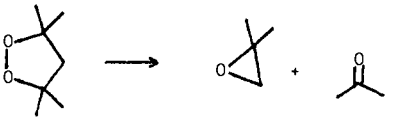
Rate constants for decompositions of **2** and **7** at various temperatures with an initial concentration of 0.5 M are listed in Table III.[9] Rate constants were also determined for decomposition of **2** at 73 °C with initial concentrations of 0.13, 0.10, 0.050, and 0.025 M. Each determination gave the same rate within the precision of the measurements (±4%).[11] In the presence of inhibitors[12] (nitrobenzene, styrene, BHT, acrylonitrile, methyl methacrylate) (0.5 M), decomposition of **2** at 76.0 °C is slightly *accelerated* (8.37 to 10.07 $\times 10^{-5}$ s^{-1}). Similarly for **7** at 130.0 °C, nitrobenzene (0.5 M) has no effect on decomposition rate while BHT (0.5 M) causes a slight *increase* (6.77×10^{-5} s^{-1}). These results probably reflect the effect of the protic or polar character of the inhibitors. The failure to observe rate *decreases* in the presence of inhibitors or at lower initial concentrations suggests the absence of induced radical-chain reactions[12] in decompositions of **2** and **7** in cyclohexane-d_{12}. Activation parameters calculated from the rate constants listed in Table III are given in Table IV together with parameters for thermal decomposition of tetramethyl-1,2-dioxolane (**11**)[13] and *tert*-butyl peroxide.[14]

As expected for a reaction involving rate determining homolysis of the peroxide bond, the activation entropy for thermal decomposition of *tert*-butyl peroxide in cyclohexane is +15 to +21 eu.[14] The rate of this nonpolar process shows only a small dependence on solvent polarity.[14] A similarly small solvent dependence of the rate and an identical $\Delta G^{\ddagger}$ are found for the **2** → **9** rearrangement.[6] However, the large *negative* activation entropy found for the latter rearrangement (i.e., −19 eu) is remarkable. It seems unlikely that this low $\Delta S^{\ddagger}$ can be ascribed[15] to efficient reclosure of **12** to **2** since **2** incorporates considerable strain not found in **12.** Moreover, reclosure of a



2 **12**

corresponding intermediate from **7** should be more likely, but the activation entropy for the decomposition of **7** is neither large nor negative. Elegant studies by Adam and Duran uncovered evidence including substituent effects which supports a concerted β-scission mechanism for decomposition of tetramethyl-1,2-dioxolane (**11**).[9] This reaction, which affords major products **13** and **14** analogous to **9**, also exhibits a large negative activation entropy (i.e., −24 eu in benzene).[9] It was



11 **13** **14**

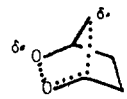
speculated that only very specific conformations of this flexible peroxide are appropriate for concerted β scission and that the low activation entropy might be explained in terms of the low

Table IV. Activation Parameters for Decomposition of Dialkyl Peroxides

peroxide	reaction solvent	reaction temp, °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mol[a]	ref
2	cyclohexane-d_{12}	57–76	20.7 ± 1.8	−19 ±5	30.2	*b*
7	cyclohexane-d_{12}	120–150	33.1 ± 1.2	3 ± 3	31.4	*b*
11	benzene	190–218	27.0 ± 1.0	−24.0 ± 2.0	39.4	13
	cyclohexane	120–135	40.8 ± 2.2 38.4	21.1 ± 1.4 15.2	30.3 30.8	14a 14b

[a] Calculated at 500 K (this work). [b] This work.

probability of achieving the appropriate conformation.[9] Such an explanation cannot be operative for decomposition of **2** since this strained bicyclic peroxide is conformationally rigid. Nevertheless, the similarity of reaction products and activation entropies suggest that the **2** → **9** rearrangement might also involve homolysis of the O-O bond with concerted β scission of a C-C bond in the transition state as indicated in **15.**



15

Geometric constraints imposed by the rigid bicyclic structure of the peroxide **2** should weaken the O-O bond owing to strain and unfavorable juxtaposition of vicinal nonbonding electron pairs on oxygen. Indeed, $\Delta H^{\ddagger}$ is considerably lower for nonpolar decomposition of **2** (21 kcal mol^{-1}) than for *tert*-butyl peroxide (38-41 kcal mol^{-1}). However, unexpectedly high thermal stability for **2**, as for **11**, is associated with an extraordinarily large negative activation entropy.

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Daniel J. Coughlin, Robert G. Salomon*

Department of Chemistry, Case Western Reserve University Cleveland, Ohio 44106

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Electrochemical Study of the Generation and Fate of Iron Dinitrosyl, a Powerful Catalyst for C–C Bond Formation from Dienes

Sir:

The building up of a selective catalyst remains a challenge to anyone interested in homogeneous catalysis. Vacant sites as well as specific ancillary ligands are needed. Reductive elimination of appropriate ligands has been proposed for the first purpose[1] and for the second one nitrosyl ligands were suggested owing to their electronic properties.[2] In this respect iron nitrosyl complexes exhibit a new selectivity toward the cyclodimerization of dienes.[3] For example $Fe(CO)_2(NO)_2$, $Fe(\eta\text{-}C_3H_5)(CO)_2NO$,[4] $[Fe(NO)_2Cl]_2 + C_2H_5MgBr$,[5] $[Fe(NO)_2Cl]_2 + (C_3H_5)_2Sn$,[6] $Na[Fe(CO)_3NO] + [M(NO)_2X]_2$ (M = Fe, Co; X = Cl, Br, I),[7] $[Fe(NO)_2Cl]_2 + Ni(CO)_4$,[8] and $[Fe(NO)_2Cl]_2 + Zn$[9] convert selectivity butadiene to 4-vinylcyclohexene. The catalytic species has been claimed to be "$Fe(NO)_2$" without further characterizations owing to the complexity of the reaction medium. The generation and the identification of this moiety has retained our attention for two purposes: (i) the chemistry of dinitrosyl complexes[2c,10] and (ii) the economical importance of 4-vinylcyclohexene as a styrene precursor.[11] The complex $[Fe(NO)_2Cl]_2$ is a valuable precursor as a one-electron reduction can lead to "$Fe(NO)_2$".[12] The reduction can be achieved chemically and electrochemically. The electrochemistry, in nonaqueous solvents, of some related nitrosyl iron complexes has already been reported.[13] However, no electrochemical data on $[Fe(NO)_2Cl]_2$ are available and, more generally, connections between electrochemistry and catalysis are scarcely described.[14] We report here on the electrochemical behavior of $[Fe(NO)_2Cl]_2$ in association with catalysis in the cyclodimerization of norbornadiene (ndb), isoprene (is), and butadiene (bd). Comparison between catalytic runs performed in the electrochemical cell and by reduction with Zn definitely proves that the moiety "$Fe(NO)_2$"[12] is the active species.

All of the experiments were carried out in deoxygenated tetrahydrofuran (thf). The dissolution of the dimer $[Fe(NO)_2Cl]_2$ occurs instantaneously leading to the paramagnetic

Scheme I[a]

$$[Fe(NO)_2Cl]_2 \longrightarrow 2Fe(NO)_2ClS_n \quad (1)$$

$$Fe(NO)_2ClS_n \rightleftharpoons [Fe(NO)_2S_n]^+Cl^- \quad (2)$$

oxidation

A wave:

$$2Fe(NO)_2ClS_n + 2Hg \xrightarrow{-4e^-} 2Fe^{2+} + 4NO + Hg_2Cl_2 \quad (3)$$

reduction

B wave:

$$Fe(NO)_2ClS_n \xrightarrow{e^-} Fe(NO)_2S_n + Cl^- \quad (4)$$

$$Fe(NO)_2ClS_n + Cl^- \longrightarrow [Fe(NO)_2Cl_2]^- \quad (5)$$

C wave:

$$[Fe(NO)_2Cl_2]^- \xrightleftharpoons{e^-} [Fe(NO)_2Cl_2]^{2-} \quad (6)$$

$$[Fe(NO)_2Cl_2]^{2-} \longrightarrow Fe(NO)_2S_n + 2Cl^- \quad (7)$$

D wave:

$$[Fe(NO)_2Cl_2]^{2-} \xrightarrow{e^-} [Fe(NO)_2Cl_2]^{3-} \quad (8)$$

$$[Fe(NO)_2Cl_2]^{3-} \longrightarrow [Fe(NO)_2S_n]^- + 2Cl^- \quad (9)$$

E wave:

$$Fe(NO)_2S_n \xrightleftharpoons{e^-} [Fe(NO)_2S_n]^- \quad (10)$$

[a] S_n represents molecules of tetrahydrofuran as ligands.

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