4a: ^{13}C NMR 77.20 (d), 69.98 (s), 59.63 (q), 57.13 (d), 27.31 (t), 25.04 (t), 19.12 (t), 17.26 (q).

4b: ^{13}C NMR: 75.15 (d), 68.22 (s), 63.19 (d), 56.71 (q), 27.05 (t), 24.13 (t), 18.83 (t), 16.88 (q).

Both diastereomers, separated with base line resolution by GC/MS (50 °C/15 min/5 °C/200° C), produced identical mass spectra: EIMS, *m/e* 127 (2), 85 (100); CI/NH$_3$, *m/e* 160 (5, M + 18), 143 (60, M + 1), 85 (100).

2-Methoxy-2-vinylcyclopentanol (5). This compound was isolated from the reaction of 1 with 3 at room temperature: ^{1}H NMR 5.89 (dd, J_1 = 17 Hz, J_2 = 11 Hz, 1 H), 5.5–5.3 (m, 2 H), 3.85 (brs, 1 H), 3.15 (s, 3 H), 2.1–1.5 (m, 6 H); ^{13}C NMR 137.07 (d), 119.18 (t), 89.32 (s), 78.68 (d), 50.66 (q), 31.28 (t), 27.62 (t), 19.70 (t); EIMS, *m/e* 143 (0.08, M + 1), 142 (0.05, M$^+$), 141 (0.2, M–1), 85 (100); CI/NH$_3$, *m/e* 160 (5, M + 18), 143 (1, M + 1), 142 (2, M$^+$), 86 (100); high-resolution (CI/NH$_3$), *m/e* 143.10712 (calcd for $C_8H_{15}O_2$ 143.10682)

2-Methoxy-1-(1-methoxyethyl)cyclopentanol (6). This compound was isolated from the reaction of 1 with 2 at room temperature: ^{1}H NMR 3.48 (q, J = 5 Hz, 1 H), 3.30 (d, J = 3 Hz, 1 H), 3.22 (s, 3 H), 3.14 (s, 3 H), 1.60 (m, 4 H), 1.35 (m, 2 H), 0.96 (d, J = 5 Hz, 3 H); ^{13}C NMR 87.03 (d), 85.43 (s), 76.22 (d), 56.24 (q), 56.04 (q), 31.91 (t), 27.55 (t), 20.44 (t), 12.81 (q); EIMS, *m/e* 142 (10), 59 (100); CI/NH$_3$, *m/e* 192 (3, M + 18), 175 (99, M + 1), 157 (100); high-resolution (CI/NH$_3$), *m/e* 175.1334 (calcd for $C_9H_{19}O_3$ 175.1331)

(*E*)-2-[(Methoxymethyl)methylene]cyclopentanol (7a) and (*Z*)-2-[(Methoxymethyl)methylene]cyclopentanol (7b). These isomers were isolated from the reaction of 1 with 3 at room temperature.

7a: ^{1}H NMR (80 MHz) 5.66 (dd, J = 5, 1 Hz, 1 H), 4.71 (brs, 1 H), 4.18 (m, 2 H), 3.47 (s, 3 H), 2.2–1.3 (m, 6 H); ^{13}C NMR 149.47 (s), 119.34 (d), 75.06 (d), 69.87 (t), 57.95 (q), 34.97 (t), 26.75 (t), 21.55 (t); EIMS, *m/e* 127 (9), 110 (42), 97 (36), 67 (100); CI/NH$_3$, *m/e* 143 (5, M + 1), 142 (20, M$^+$), 125 (100).

7b: ^{1}H NMR (80 MHz) 5.65 (brs, 1 H), 4.40 (brs, 1 H), 3.93 (dd, J = 7, 1 Hz, 2 H), 3.30 (s, 3 H), 2.2–1.3 (m, 6 H); ^{13}C NMR 151.76 (s), 120.03 (d), 70.91 (d), 69.56 (t), 57.82 (q), 35.53 (t), 32.28 (t), 22.87 (t); EIMS, *m/e* 127 (2), 110 (34), 97 (80), 67 (100); CI/NH$_3$, *m/e* 143 (2, M + 1), 142 (23, M$^+$), 125 (100).

Acknowledgment. This work was supported by grants from the Univeristy of Kansas General Research Fund and the Institute of General Medical Sciences (GM 7775) of the National Institutes of Health. We are indebted to Dr. Grover Everett, Dr. Joseph Heppert, and Dr. Richard Schowen for many helpful discussions and also thank Robert Drake and Charles Judson for acquisition of the mass spectral data.

Registry No. 1, 65656-91-9; 2, 1600-27-7; 3, 10045-94-0; 4a, 108269-05-2; 4b, 108341-60-2; 5, 108269-06-3; 6, 108269-07-4; 7a, 108269-08-5; 7b, 108269-09-6; CH$_3$OH, 67-56-1; 1-vinylcyclopentanol, 28638-58-6.

Oxidation of *o*-Nitrobenzeneselenenic Acid by Hydrogen Peroxide in Alkaline Solution[1]

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In contrast to most other areneselenenic acids (ArSeOH), solutions of *o*-nitrobenzeneselenenic acid, **1a** (Ar = *o*-$O_2NC_6H_4$) are sufficiently stable that study of the mechanisms of its reactions can be done in a straightforward fashion. The objective of this and earlier studies[2] has been to use **1a** as a substrate to obtain information about the the mechanisms of some of the principal reactions of areneselenenic acids.

Table I. Kinetics of the Oxidation of *o*-Nitrobenzeneselenenic Acid by Hydrogen Peroxide in Neutral and Alkaline Solution in Water at 25 °C[a]

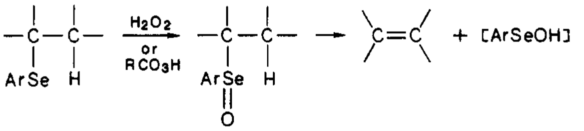
buffer or solution	pH[b]	$k_1/C_{H_2O_2}$,[c] $M^{-1}\ s^{-1}$
0.05 M KH_2PO_4 plus 0.014 M NaOH	6.5	0.0041 ± 0.0001
0.05 M KH_2PO_4 plus 0.029 M NaOH	7.0	0.0131 ± 0.0005
0.05 M KH_2PO_4 plus 0.041 M NaOH	7.5	0.029 ± 0.003
0.05 M KH_2PO_4 plus 0.0467 M NaOH	8.0	0.086 ± 0.002
0.025 M $NaHCO_3$ plus 0.004 M NaOH	9.5	3.26 ± 0.06
0.025 M $NaHCO_3$ plus 0.011 M NaOH	10.0	7.5 ± 0.4
0.025 M $NaHCO_3$ plus 0.018 M NaOH	10.5	9.5 ± 0.2
0.025 M Na_2HPO_4 plus 0.005 M NaOH	11.1	11.4 ± 0.6
0.025 M Na_2HPO_4 plus 0.011 M NaOH	11.5	8.3 ± 0.6
0.025 M Na_2HPO_4 plus 0.027 M NaOH	12.0	3.9 ± 0.2
0.032 M NaOH	12.5	1.74 ± 0.08
0.10 M NaOH	13.0	0.43 ± 0.02

[a] Initial concentration of **1a**, 0.0001 M; $C_{H_2O_2}$ from 0.004 to 0.008 M. [b] pHs of buffer solutions are from *Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, p D-148. [c] Average of from two to four runs at each pH.

Oxidation of an areneselenenic acid to the corresponding seleninic acid by a peracid or hydrogen peroxide (eq 1) is

$$\mathrm{ArSeOH} \xrightarrow[\mathrm{or}\ \mathrm{RCO_3H}]{\mathrm{H_2O_2}} \mathrm{ArSeO_2H} \qquad (1)$$

a reaction that is important as an adjunct to the synthetically useful formation[3] of alkenes by oxidative elimination of alkyl aryl selenides (eq 2). It is customary to



(2)

employ a sufficient excess of oxidant so that the selenenic acid liberated in eq 2 is oxidized to the seleninic acid and is thereby prevented from adding to the alkene double bond (ArSeOH + >C=C< → >(ArSe)C–C(OH)<).

In previous work[2b] the mechanism of the oxidation of **1a** by hydrogen peroxide in acid solution was determined. The present paper deals with the mechanism of the much more rapid oxidation that takes place in alkaline solution.

Results and Discussion

Preliminary experiments revealed that **1a** is oxidized by hydrogen peroxide in alkaline solution much faster than in acid solution. Isolation of *o*-$O_2NC_6H_4SeO_2H$ in 80% yield after acidification of the reaction solution established that the stoichiometry of the oxidation was the same.

The kinetics of the oxidation were studied in water at 25 °C in a series of buffers and dilute sodium hydroxide solutions covering a pH range from 6.5 to 13.0. Hydrogen peroxide (0.004–0.008 M) was present in large stoichiometric excess over **1a** (10^{-4} M). At pHs below the pK_a of **1a** (10.4)[4] the progress of the oxidation was monitored at λ_{max} for *o*-$O_2NC_6H_4SeOH$; at higher pHs the λ_{max} for the anion of **1a**, *o*-$O_2NC_6H_4SeO^-$, was used. At either wavelength plots of log $(A - A_\infty)$ vs. time were linear. At each

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[1] This research was supported by the National Science Foundation, Grant CHE-85-19055.

(2) (a) Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *J. Org. Chem.* 1984, *49*, 3106. (b) Kice, J. L.; Chiou, S.; Weclas, L. *Ibid.* 1985, *50*, 2508. (c) Kang, S.-I.; Kice, J. L. *Ibid.* 1986, *51*, 295.

(3) For reviews of the oxidative elimination of selenides and its use in synthesis, see: (a) Reich, H. J. *Acc. Chem. Res.* 1979, *12*, 22. (b) Clive, D. L. J. *Tetrahedron* 1978, *34*, 1049.

(4) Kang, S.-I.; Kice, J. L. *J. Org. Chem.* 1986, *51*, 287.

0022-3263/87/1952-2953$01.50/0

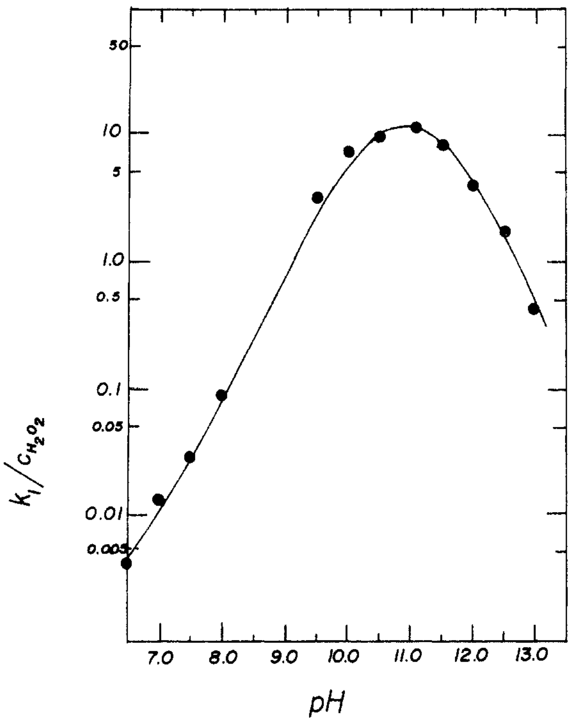


Figure 1. pH–rate profile for oxidation of **1a** by hydrogen peroxide in water at 25 °C: ●, experimental results; solid curve calculated from eq 4 using $pK_a = 10.4$, $pK_{H_2O_2} = 11.5$, and $k_{H_2O_2}' = 20\ M^{-1}\ s^{-1}$, and assuming that $k_{H_2O_2}$ (eq 7) equals $0.002\ M^{-1}\ s^{-1}$ and is independent of pH.

pH the experimental first-order rate constants, k_1, were proportional to $C_{H_2O_2}$, showing that the reaction was first order in hydrogen peroxide. The average value of $k_1/C_{H_2O_2}$ at each pH is listed in Table I, and the pH–rate profile is shown in Figure 1.

If eq 3a and/or 3b are the only reactions that are important kinetically for the oxidation of **1a** by hydrogen peroxide in alkaline solution the dependence of $k_1/C_{H_2O_2}$ on pH will be

$$ArSeO^- + H_2O_2 \xrightarrow{k'_{H_2O_2}} ArSeO_2H + OH^- \qquad (3a)$$

$$ArSeO_2H \xrightarrow{fast} ArSeO_2^- + H_2O$$

$$ArSeOH + HO_2^- \xrightarrow{k_{HO_2^-}} ArSeO_2H + OH^- \qquad (3b)$$

$$k_1/C_{H_2O_2} = \frac{(k'_{H_2O_2}K_a + k_{HO_2^-}K_{H_2O_2})a_{H^+}}{K_aK_{H_2O_2} + (K_a + K_{H_2O_2})a_{H^+} + a_{H^+}^2} \qquad (4)$$

where K_a and $K_{H_2O_2}$ are the acid dissociation constants for the selenenic acid and H_2O_2, respectively. At lower pHs where $a_{H^+}^2$ is the largest of the three terms in the denominator, $k_1/C_{H_2O_2}$ will be proportional to $1/a_{H^+}$, and the rate will increase with increasing pH. At the most alkaline pHs $K_aK_{H_2O_2}$ becomes the largest term in the denominator, $k_1/C_{H_2O_2}$ is proportional to a_{H^+}, and the rate decreases with increasing pH. The maximum in the rate will occur at pH $^1/_2(pK_a + pK_{H_2O_2})$ or at pH 11. The pH–rate profile in Figure 1 is in accord with these expectations.

Which is the primary contributor to the rate, eq 3a or eq 3b? The kinetic behavior of the oxidation of the corresponding methyl ester, $o\text{-}O_2NC_6H_4SeOCH_3$ (**2a**), provides the answer. Reaction of HO_2^- with both $ArSeOCH_3$ and ArSeOH (eq 3b) would be expected to proceed at similar rates; but, since **2a** lacks the ionizable proton on oxygen, a reaction analogous to eq 3a is not possible for the ester. If eq 3b is the reaction primarily responsible for the facile oxidation of **1a**, oxidation of **2a** under the same conditions would be expected to show a similar rate and pH dependence. On the other hand, if it is eq 3a, oxidation of **2a** should be much slower and not show the type of dependence of $k_1/C_{H_2O_2}$ on pH observed with **1a**.[5]

Because of the lack of solubility of the ester in water, the comparison of the kinetic behavior of the oxidations of **2a** and **1a** was carried out in 50% acetonitrile. To avoid complications from the alkaline hydrolysis of **2a** ($ArSeOCH_3 + OH^- \rightarrow ArSeO^- + CH_3OH$), measurements were restricted to buffers with pHs near neutrality (7.0–8.0). Values of $k_1/C_{H_2O_2}$ for **1a** and **2a** under these conditions were as follows

for **1a**

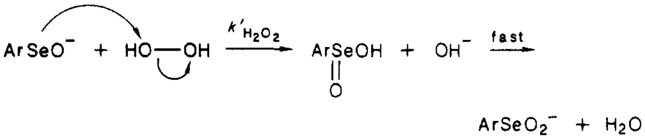
$$k_1/C_{H_2O_2}\ (M^{-1}\ s^{-1}) = 0.0020 + (4.4 \times 10^{-10})(1/a_{H^+}) \qquad (5a)$$

for **2a**

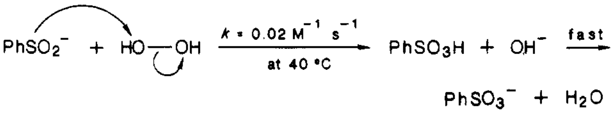
$$k_1/C_{H_2O_2}\ (M^{-1}\ s^{-1}) = 0.0013 + (0.06 \times 10^{-10})\ (1/a_{H^+}) \qquad (5b)$$

The rates (0.0020 and 0.0013 $M^{-1}\ s^{-1}$) for the pH-independent component of $k_1/C_{H_2O_2}$ show that the un-ionized substrates (ArSeOH and $ArSeOCH_3$) react with H_2O_2 at similar rates. On the other hand, the pH-dependent term, corresponding to reaction by the pathways of eq 3, is 75 times larger for **1a** than for **2a**. This establishes that it is eq 3a, rather than 3b, that is responsible for the facile oxidation of **1a** by hydrogen peroxide in alkaline solution shown in the pH–rate profile in Figure 1.

Equation 3a presumably takes place by nucleophilic attack of the selenenate anion on one of the oxygen atoms in H_2O_2:



Its rate at 25 °C ($k_{H_2O_2}' = 20\ M^{-1}\ s^{-1}$) is 10^3 times faster than the rate for the analogous oxidation of $PhSO_2^-$ by H_2O_2 at 40 °C (eq 6).[6] The much higher reactivity of



(6)

$o\text{-}O_2NC_6H_4SeO^-$ as a nucleophile as compared to $PhSO_2^-$ is not surprising. An arenesulfenate ion ($ArSO^-$) has been shown to be 3×10^4 more reactive as a nucleophile than the corresponding arenesulfinate ($ArSO_2^-$).[7]

The present study also shows that the rate constant for eq 3a ($k_{H_2O_2}'$) is 6000 times larger than the rate constant ($k_{H_2O_2}$) at which the undissociated selenenic acid reacts with hydrogen peroxide (eq 7). This indicates why addition

$$ArSeOH + H_2O_2 \xrightarrow{k_{H_2O_2}} ArSeO_2H + H_2O \qquad (7)$$

of a base to the reaction mixture may be beneficial in oxidative eliminations (eq 2) in which it is important to remove the selenenic acid produced as rapidly as possible.

Experimental Section

Preparation and Purification of Reagents. *o*-Nitrobenzeneselenenic acid (**1a**) was prepared from ethyl *o*-nitrophenyl

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[5] For a general discussion of this approach to distinguishing between mechanisms in suitable acid- and base-catalyzed reactions, see: Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969; pp 188–190.

[6] Lindberg, B. J. *Acta Chem. Scand.* **1966**, *20*, 1843.

[7] Boduszek, B.; Kice, J. L. *J. Org. Chem.* **1982**, *47*, 3199.

selenide in the manner described by Kang and Kice.[2c] Once prepared **1a** was dissolved in 50% acetonitrile and the solution (10^{-2} M in **1a**) was stored in the refrigerator until used, but in no event for longer than 1 day. Methyl *o*-nitrobenzeneselenenate (**2a**) was prepared from **1a** by the procedure outlined in the same paper[2c] and was purified by recrystallization from methanol, mp 52–53 °C. Hydrogen peroxide (Mallinckrodt, 30% aqueous solution) was used without further purification. Acetonitrile (Aldrich, spectrophotometric grade) was redistilled before use. All water used in the kinetic runs was doubly distilled from glass.

Procedure for Kinetic Runs. An aqueous solution (3.5 mL) containing the desired concentration of buffer (or sodium hydroxide) was placed in a 1-cm cell in the thermostated cell compartment of a Beckmann Model DU-50 spectrophotometer. To this solution was then first added 35 μL of a 10^{-2} M solution of **1a** in 50% acetonitrile. This was followed by the addition via a second microsyringe of the desired amount (10–20 μL) of a 1.5 M solution of hydrogen peroxide in water. The progress of the oxidation was then monitored by following the decrease in the absorbance of the solution at either 420 nm (for runs at pH $\leq$10.0) or 550 nm (for runs at pH $\geq$10.5).

The procedure for the kinetic runs in 50% acetonitrile was similar. With **2a** a 10^{-2} M stock solution in *anhydrous* acetonitrile was used. The progress of the oxidation of the ester was followed at 410 nm, that of **1a** at 422 nm.

Products of the Oxidation of 1a in Alkaline Solution. To confirm that *o*-nitrobenzeneseleninic acid is the product formed when **1a** is oxidized by H_2O_2 in alkaline solution, 0.037 g (0.17 mmol) of **1a** was dissolved in 5 mL of purified tetrahydrofuran and 1 mL of aqueous 0.1 M sodium hydroxide was added, followed by 0.10 mL of aqueous 30% hydrogen peroxide. The solution was allowed to stand at room temperature for 2 h and then acidified by the addition of 1.5 mL of 0.1 M perchloric acid. Most of the solvent was removed under reduced pressure at room temperature and the precipitate that separated was filtered off, washed with cold water followed by a little cold ether, and dried under vacuum, yielding 0.032 g (79%) of *o*-nitrobenzeneseleninic acid, mp 179–182 °C, identical in all respects with a known sample prepared by the procedure of Behaghel and Seibert.[8]

Registry No. **1a**, 56790-59-1; **1a** (anion), 108366-29-6; **1a** (methyl ester), 108366-30-9; H_2O_2, 7722-84-1; KH_2PO_4, 7778-77-0; $NaHCO_3$, 144-55-8; Na_2HPO_4, 7558-79-4; NaOH, 1310-73-2.

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[8] Behaghel, O.; Seibert, H. *Chem. Ber.* **1933**, *66*, 708.

On the Existence of *trans*-Cyclohexene

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Cis $\rightleftharpoons$ trans isomerization is a commonly observed reaction of photochemically excited olefins. In the case of small-ring cycloolefins, the trans isomer is more strained than the cis isomer, and this higher ring strain may lead to enhanced chemical reactivity.

The smallest stable cyclic trans olefin is *trans*-cyclooctene.[2] *trans*-Cycloheptene has also been prepared, but at 1 °C it reverts to the cis isomer with a half-life of ca. 10 min.[3] From the lifetimes at various temperatures Inoue et al.[3] estimated a $\Delta H^{\ddagger}$ of ca. 17 kcal/mol for the isomerization. The intermediacy of *trans*-cyclohexene (**1**) in reactions of *cis*-cyclohexene (**2**) has frequently been postulated.[4] However, no indications for the existence of *trans*-cyclohexene as a discrete chemical species have been reported to date, although Joussot-Dubien et al. obtained evidence for the formation of 1-phenyl-*trans*-cyclohexene upon flash pyrolysis of the cis isomer.[5] Because experimental detection of **1** is bound to be difficult, we decided to address this problem from a theoretical point of view.

From molecular mechanics calculations, Allinger and Sprague predicted **1** to be 42 kcal/mol less stable than **2**. They did not carry out a full optimization of the transition state for the trans → cis isomerization, but a reaction path calculation produced an estimated barrier of ca. 13 kcal/mol.[6] Maier and Schleyer concluded that **1** does not exist on the basis of MNDO calculations including a limited CI.[7] It has been noted before that MNDO adventitiously produces correct cis $\rightleftharpoons$ trans isomerization barriers *without* the use of CI.[8] Inclusion of CI will thus result in an artificially low barrier or no barrier at all.[9] However, **1** does correspond to a local minimum at the closed-shell RHF/MNDO level.[7,10] We now report ab initio calculations on **1**, **2**, and the transition-state **3** for the isomerization **1** → **2**, which we believe provide a definitive answer to the question of the existence of **1**.

trans-Cyclohexene will have a large amount of torsion strain at the C_1C_2 double bond. Both it and its cis isomer will presumably have C_2 symmetry, but the isomerization **1** → **2** is forbidden in this symmetry. Thus, a correct zeroth-order description requires at least a two-configuration wave function; in this work we have employed an equivalent GVB formalism,[11] using one pair function for the C_1C_2 π-bond. The geometries of **1**–**3** were optimized[12]

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[1] Part of the forthcoming Ph.D. Thesis of P. J. J. A. Timmermans, Utrecht.

[2] See, e.g.: Cope, A. C.; Pike, R. A.; Spencer, C. F. *J. Am. Chem. Soc.* **1953**, *75*, 3212. See also ref 16.

[3] Inoue, Y.; Ueoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* **1983**, 983 and references cited therein.

[4] Salomon, R. G.; Folting, K.; Streib, W. E.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1145. Timmermans, P. J. J. A.; de Ruiter, G. M. J.; Tinnemans, A. H. A.; Mackor, A. *Tetrahedron Lett.* **1983**, *24*, 1419 and references cited therein.

[5] Bonneau, R.; Joussot-Dubien, J.; Salem, L.; Yarwood, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 4329. Dauben, W. G.; v. Riel, H. C. H. A.; Leroy, F.; Joussot-Dubien, J.; Bonneau, R. *J. Am. Chem. Soc.* **1980**, *101*, 1901.

[6] Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734.

[7] Maier, W. F.; Schleyer, P. v. R. Presented at the 5th IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, Aug. 17–22, 1980.

[8] Dewar, M. J. S.; Merz, K. M., Jr. *J. Chem. Soc., Chem. Commun.* **1985**, 343.

[9] In C_2 symmetry, the ground-state of 1 correlates with an excited state of 2. This means that a realistic closed-shell description of the isomerization process is impossible. In MNDO calculations, a "minimal CI" is frequently used to avoid this problem. This minimal CI is just a way to arrive at a (more or less) correct zeroth-order wave function within the MNDO formalism (in our ab initio calculations we have used a two-configuration wave function for the same purpose). The minimal CI avoids the unrealistically sharp peaking of the energy associated with the closed-shell description of a forbidden process; since the minimal-CI contribution is large near the transition state but much smaller for reactant and product, it will *always* lower the calculated activation energy. In contrast, the *subsequent* application of a *large-scale CI* to a *correct* (*two-configuration*) *zeroth-order wave function* can improve the description of reactant, transition state and product equally well and can therefore *increase or decrease* the activation energy.

[10] Budzelaar, P. H. M., unpublished results.

[11] Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368.

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