

Rates and Mechanism in the Electron Transfer Mediated Reduction of *N*-Chlorosuccinimide by Succinimide Anion

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The electrochemical reduction of *N*-chlorosuccinimide in acetonitrile at a platinum cathode parallels the reduction of *N*-bromosuccinimide.¹ The overall *n* value is 1; the succinimide anion, generated by a two-electron reduction of *N*-chlorosuccinimide, is an intermediate; homogeneous electron transfer from the succinimide anion to *N*-chlorosuccinimide generates the succinimidyl radical, which is the precursor for the products formed. The reduction of *N*-chlorosuccinimide by the succinimide anion, added as a quaternary ammonium succinimide, in a homogeneous chemical system is significantly different from the comparable reaction with *N*-bromosuccinimide. Rate constants for the pertinent reactions have been measured, and the reaction mechanism has been discussed.

The electrochemical reduction of *N*-bromosuccinimide (SBr) in acetonitrile (AN) at a platinum cathode generates the succinimidyl radical (S \cdot) in an overall process for which the *n* value is 1, where *n* is the number of faradays of charge passed per mole of reaction. The overall reaction is shown in eq 1, and the steps involved are given by eq 2a and 2b. The succinimide anion (S $^-$), generated by



two-electron reduction of SBr, is an intermediate in this process, and this can be demonstrated by trapping experiments in which the anion is captured by alkylating agents, e.g., methyl tosylate, to give *N*-alkylsuccinimides. With increasing capture of the anion the *n* value for the electrochemical reduction approaches 2 as a limit.¹

Electron transfer from S $^-$ to SBr generates the succinimidyl radical, S \cdot , as shown in eq 2b, and this reaction was also studied in a homogeneous system with S $^-$ added as tetra-*n*-butylammonium succinimide (TBAS). Measurements of the rate of this reaction indicated that it is not a simple, second-order reaction between SBr + S $^-$. It involves the prior, rapid formation of a complex (C), between SBr and S $^-$, which then undergoes electron transfer in a rate-determining step to form S \cdot , as indicated in eq 3 and 4.¹ This complex, C, has been prepared.² It is



stable in the solid state for a limited period of time (2 or more weeks at room temperature), and its properties and reactions are consistent with the reaction mechanism indicated by eq 3 and 4.²

The reduction of *N*-chlorosuccinimide (SCL), effected both electrochemically and by electron transfer from S $^-$, shows many of the characteristics observed in the reduction of SBr. But there are some significant differences, and these are of sufficient importance to justify a detailed exposition of the results. In what follows, the reduction

of SCL (1) by electrolysis at a platinum cathode and (2) by electron transfer from S $^-$ will be described. Reaction rates will be given where pertinent, and the reaction mechanisms will be discussed.

Results and Discussion

Voltammetry experiments indicate that the reduction of SCL requires a more negative potential than that found for SBr. At a platinum electrode in AN, containing 0.25 M tetra-*n*-butylammonium fluoborate (TBAF) as the supporting electrolyte, and at a potential scan rate of 200 mV s $^{-1}$, the reduction wave for 0.005 M SCL gave $E_p = -0.65$ V vs. Ag/Ag $^+$ (0.1 M).³ This is to be compared with the E_p value of +0.03 V vs. SCE (~ -0.25 V vs. Ag/Ag $^+$ (0.1 M)) reported for SBr.¹ At a glassy carbon electrode the reduction potential for SCL is shifted to a more negative value ($E_p = -0.80$ V vs. Ag/Ag $^+$ (0.1 M)). At both electrodes the process is irreversible, with no oxidation wave for the reduction product detectable even at sweep rates of 100 V s $^{-1}$.

For preparative electrolyses in AN containing 0.25 M TBAF, the potential of the working cathode was maintained in the range -0.8 to -1.0 V vs. Ag/Ag $^+$ (0.1 M). Coulometry on a typical experiment with the initial SCL concentration at 0.072 M gave an *n* value of 0.98 F/mol. The amount of chloride ion formed was determined by a GC method,⁴ in which *n*-butyl tosylate was added to a portion of the electrolyzed solution and chloride ion was then determined by GC as *n*-butyl chloride. The yield of chloride ion was 93%. The yield of succinimide (SH) was determined both by GC and by measuring the intensity of the N-H band at 3280 cm $^{-1}$. The value obtained by GC was 64%, while the infrared method provided the lower value of 45%.⁵ When SCL was electrolyzed as above but in the presence of excess methyl tosylate (molar ratio methyl tosylate/SCL = 9.7), the SH yield, determined both by GC and infrared, was reduced to 8% and *N*-methylsuccinimide was formed in 85% yield. Integration of the current-time curve for this experiment provided an *n* value of 1.81 F/mol., whereas the product yields above indicate an *n* value of 1.86 F/mol.

(3) At platinum on the reverse, anodic scan one observes oxidation of chloride ion with $E_p \approx +1.25$ V vs. Ag/Ag $^+$ (0.1 M).

(4) Moore, W. M. *Anal. Chem.* 1982, 54, 602.

(5) The values obtained by infrared measurements are probably more reliable. A significant portion of the product is a succinimide polymer, and this may decompose in part under the GC conditions.

(1) Barry, J. E.; Finkelstein, M.; Moore, W. M.; Ross, S. D.; Ebersson, L.; Jonsson, L. *J. Org. Chem.* 1982, 47, 1292.

(2) Barry, J. E.; Finkelstein, M.; Moore, W. M.; Ross, S. D.; Ebersson, L. *Tetrahedron Lett.* 1984, 25, 2847.

Table I. Rate Constants for the Reaction of *N*-Chlorosuccinimide and Succinimide Anion in Acetonitrile at 1 ± 1 °C

| [SCl] | [S ⁻] | [S ⁻] ₀ /[SCl] ₀ | <i>k</i> ₁ , M ⁻¹ s ⁻¹ |
|---------|-------------------|--|---|
| 0.0255 | 0.0103 | 0.403 | 0.21 |
| 0.0248 | 0.0102 | 0.412 | 0.21 |
| 0.0105 | 0.00502 | 0.495 | 0.24 |
| 0.0175 | 0.0102 | 0.581 | 0.19 |
| 0.0103 | 0.0103 | 1.00 | 0.15 |
| 0.0103 | 0.0103 | 1.00 | 0.16 |
| 0.0103 | 0.0103 | 1.00 | 0.17 |
| 0.0104 | 0.0104 | 1.00 | 0.16 |
| 0.0225 | 0.0225 | 1.00 | 0.15 |
| 0.0461 | 0.0470 | 1.02 | 0.17 |
| 0.0459 | 0.0470 | 1.02 | 0.17 |
| 0.0102 | 0.0153 | 1.49 | 0.11 |
| 0.0102 | 0.0153 | 1.49 | 0.10 |
| 0.00503 | 0.0101 | 2.00 | 0.10 |
| 0.00511 | 0.0102 | 2.00 | 0.10 |
| 0.0101 | 0.0202 | 2.00 | 0.097 |
| 0.0101 | 0.0202 | 2.00 | 0.096 |
| 0.0101 | 0.0202 | 2.00 | 0.092 |

The electrochemical results reported to this point are consistent with the reaction mechanism reported for SBr.¹ A two-electron reduction of SCl generates S⁻ and chloride ion. The succinimide anion can be trapped with methyl tosylate, yielding *N*-methylsuccinimide, but in the absence of the alkylating agent electron transfer from S⁻ to SCl generates the succinimidyl radical, which is responsible for the final products.

However, a study of the rate of reaction of SCl with S⁻ quickly pointed to significant differences. Our first measurements were made at 25 °C in AN solutions containing equivalent quantities of SCl and TBAS, with 0.25 M TBAF as the supporting electrolyte. The reaction was followed by determining SCl as a function of time at either a glassy carbon or platinum cathode. The reaction proved to be very much faster than the corresponding reaction with SBr. In an experiment with initial SCl and S⁻ concentrations at 0.021 M and 0.022 M, respectively, the reaction was 84% completed in 2.75 min. To permit more convenient and more reliable measurements of the rates, the temperature was dropped to 1 ± 1 °C. The results that were obtained are given in Table I.

The data could not be treated in a manner similar to that used in the SBr case. For runs with [SCl]₀ = [S⁻]₀ a plot of log [SCl] vs. *t* was not linear, but a plot of 1/[SCl] vs. *t* gave a straight line. This points to a second-order process for the rate-determining step. Either no SCl-S⁻ complex is involved or, if the complex is an intermediate, the rate of its decomposition exceeds the rate of its formation.

Two features of the results of Table I are significant. The reaction is not a simple, bimolecular process, since variation of the initial concentrations can change the experimentally obtained rate constant by more than a factor of 2. However, at a constant [S⁻]₀/[SCl]₀ ratio the derived rate constants are constant within experimental error even when the initial concentrations are changed more than fourfold. For the seven experiments in Table I with [S⁻]₀/[SCl]₀ equal to 1.00 or 1.02, the rate constant is 0.16 ± 0.01 M⁻¹ s⁻¹ even though the variation in the initial concentrations is as much as 4.56-fold.

As shown in Figure 1 a plot of *k* vs. [S⁻]₀/[SCl]₀ is reasonably linear. The line drawn was determined by the method of least squares. The experimental points do show some deviation from the line, but the fit is as good as can be expected, especially since the temperature control was only to ±1.0°. The rate equation, based on this treatment,

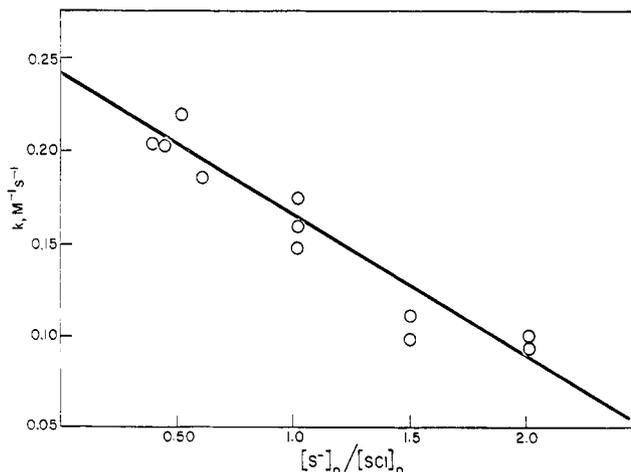


Figure 1.

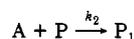
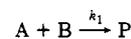
is given by eq 5, where the intercept in Figure 1 provides *k*₁ and the slope determines *k*₂.

$$-\frac{d[\text{SCl}]}{dt} = k_1[\text{SCl}][\text{S}^-] - k_2[\text{S}^-]^2 \quad (5)$$

To check the validity of eq 5 and to investigate other possible mechanisms for those reactions, a Hewlett-Packard Model HP-85 desktop computer was programmed to use the Method of Finite Differences⁶ to determine the solution for a given system of differential rate equations, given the initial concentrations and assumed values for the rate constants.⁷ The computer program made it possible to check the fit provided by any postulated mechanism and any given set of rate constants by comparing experimental vs. calculated [SCl] vs. *t* plots and by comparing the experimentally determined and calculated second-order plots and the resultant bimolecular rate constants.

(6) Riditmyer, R. D.; Morton, K. W. "Difference Methods for Initial-Value Problems", 2nd ed.; Wiley: New York, 1967; p 7.

(7) We will illustrate the method with the simple mechanism shown:



where P and P₁ are products. The differential equations involved are as follows:

$$\frac{d[\text{A}]}{dt} = k_1[\text{A}][\text{B}] - k_2[\text{A}][\text{P}]$$

$$\frac{d[\text{B}]}{dt} = k_1[\text{A}][\text{B}]$$

$$\frac{d[\text{P}]}{dt} = k_1[\text{A}][\text{B}] - k_2[\text{A}][\text{P}]$$

No equation is written for P₁, since it has no effect on the other chemical entities. For each chemical species, A, B, and P, the computer determines the concentration at each successive time increment, using the relationship (shown for A)

$$[\text{A}][t + \Delta t] = [\text{A}][t] + \frac{d[\text{A}]}{dt} \Delta t$$

Δt is the time increment and was generally taken to be 10 s. Thus, for the simulation of a 45-min experiment using 10-s intervals, 270 calculations are performed for each chemical species involved. The computer was programmed to output only the concentration of that species, the concentration of which was determined experimentally as a function of time, and at times which matched the experimental data points for a given kinetic run. In the actual mechanisms of interest that species was always SCl. The program also plots the experimental data points for [SCl], and the simulated values of [SCl], on the same scale. The second-order kinetic plot was also determined for both the experimental data and the simulated data.

Table II. Comparison of Experimental and Calculated Values of $[S\dot{C}l]_t$ for a Run with $[S\dot{C}l]_0 = 0.0101$ M and $[S^-]_0 = 0.0202$ M

| <i>t</i> , min | $[S\dot{C}l]_t$ | |
|-------------------|-----------------|--------|
| | exptl | calcd |
| 0.0 | 0.0101 | 0.0101 |
| 1.0 | 0.0078 | 0.0085 |
| 2.0 | 0.0069 | 0.0073 |
| 4.0 | 0.0056 | 0.0056 |
| 7.0 | 0.0046 | 0.0039 |
| 10.0 | 0.0036 | 0.0030 |
| 15.0 | 0.0026 | 0.0020 |
| 20.0 | 0.0018 | 0.0014 |
| 30.0 | 0.0008 | 0.0008 |

To determine the appropriateness of the rate equation 5 and to define the mechanism of the SCl-S⁻ reaction, the reaction sequence eq 6 followed by eq 7 and eq 6 followed



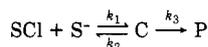
by eq 8 were considered. In both cases the rate constants, k_1 and k_2 , were those obtained from the slope and intercept of Figure 1. With eq 6 and 7 runs with $[S\dot{C}l]_0 > [S^-]_0$ gave satisfactory agreement, but for runs with $[S\dot{C}l]_0 < [S^-]_0$ and with $[S\dot{C}l]_0 = [S^-]_0$, the divergences between calculated and experimental values were unacceptable. For the sequence of reactions 6 and 8, only runs with $[S\dot{C}l]_0 = [S^-]_0$ gave a good fit.

The foregoing results suggested that a mechanism involving more than two adjustable parameters would be required to fit our results, and, in fact, one involving three rate constants provided an excellent fit. The sequence of reactions is the following:

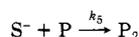
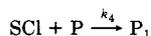


Here, P, P₁, and P₂ are products, the nature and significance of which will be discussed below. With $k_1 = 0.11$ M⁻¹ s⁻¹ and $k_2 = k_3 = 5.0$ M⁻¹ s⁻¹, representative runs with $[S\dot{C}l]_0 = [S^-]_0$, with $[S\dot{C}l]_0 > [S^-]_0$, and with $[S\dot{C}l]_0 < [S^-]_0$ all provided excellent agreement between experimental and calculated $[S\dot{C}l]_t$ values.⁸ The data for a worst case, a run with $[S\dot{C}l]_0 = 0.0101$ M and $[S^-]_0 = 0.0202$ M is shown in

(8) The more complex mechanism shown below also provides an excellent fit to our experimental data:



where C is a complex formed from SCl and S⁻.²



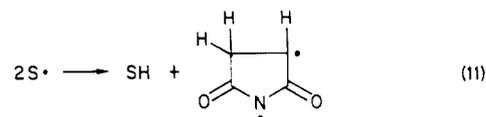
where P, P₁, and P₂ are products as noted in the body of this work. Excellent fits were obtained with $k_1 = 0.3$ M⁻¹ s⁻¹, $k_2 = 0.025$ s⁻¹, $k_3 = 0.015$ s⁻¹, and $k_4 = k_5 = 5$ M⁻¹ s⁻¹. This treatment involves five adjustable parameters, and we prefer the simpler mechanism that requires only three rate constants. One interesting facet of this mechanism is that it postulates the SCl-S⁻ complex as an unstable intermediate. The computer program permits calculation of the concentration of the complex, [C], as a function of time. For example, in the run with $[S\dot{C}l]_0 = 0.0461$ M and $[S^-]_0 = 0.470$ M the concentration of C peaks at 0.0086 M after 35 s and decays rapidly thereafter.

Table III. Comparison of Experimental and Calculated Bimolecular Rate Constants for Representative Runs

| $[S\dot{C}l]_0$ | $[S^-]_0$ | k_{exptl} , M ⁻¹ s ⁻¹ | k_{calcd} , M ⁻¹ s ⁻¹ |
|-----------------|-----------|--|--|
| 0.0104 | 0.0104 | 0.16 | 0.17 |
| 0.0461 | 0.0470 | 0.17 | 0.18 |
| 0.0105 | 0.0052 | 0.24 | 0.23 |
| 0.0101 | 0.0202 | 0.09 | 0.13 |

Table II. A better indication of the excellence of the fit is provided by a comparison of the experimental and calculated bimolecular rate constants, k , for a series of representative runs as shown in Table III.

The major products in the reactions of both SBr and SCl are succinimide and a low molecular weight succinimide polymer, in which the succinimide units are joined by both C-N and C-C linkages. The reaction path to these products is complex. Maleimide has been shown to be an intermediate, and its formation involves the cage reaction 11 of the initially generated succinimidyl radicals to form succinimide and a diradical. These results have been reported in complete detail elsewhere.⁹



A comment with respect to the nature of S⁻, as generated by the reaction between S-X and S⁻, is pertinent in view of the discussion and controversy around this subject.¹⁰ Based on our results to date, S⁻ from the S-X/S⁻ reaction has the character of S_π⁻; its reactions are limited to hydrogen atom abstraction and initiation of maleimide polymerization. There is no indication of the formation of ring-opened products, a characteristic property of S_σ⁻. The bimolecular reaction between two S_π⁻ to give the diradical (reaction 11) and, eventually, maleimide is, however, of some interest in this connection.⁹

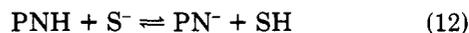
In the mechanism which we are proposing for the SCl-S⁻ reaction, reactions 6, 9, and 10, P represents the aggregate of products indicated above—the succinimide, the polymer, and any intermediates, e.g., maleimide or the diradical, which may be involved. P₁ represents any products formed by reaction of these primary products with SCl, and P₂ represents the secondary products resulting from reaction with S⁻. Since we measure the rate of disappearance of SCl, reaction 9 serves to increase that rate, but reaction 10 has the opposite effect.

The stoichiometry of the electron transfer reaction between SCl and S⁻ is 1:1. If in a reaction with excess SCl the amount of SCl consumed exceeds the initial S⁻ concentration, some side reaction involving SCl must be taking place. This is not simply a first-order decomposition of SCl, since, under our mild conditions (AN solvent at 1 ± 1 °C), SCl is stable both in AN alone and in a previous reaction mixture where $[S\dot{C}l]_0$ equaled $[S^-]_0$. For example, in a reaction with $[S\dot{C}l]_0 = 0.0410$ M and $[S^-]_0 = 0.0103$ M, the SCl concentration was 0.0298 M after 7 min and 0.0248 M after 30 min. But for 1:1 stoichiometry the reaction should have ceased when the SCl concentration was 0.0307 M, before the reaction had gone 7 min! A side reaction is clearly indicated, and the possibility that suggests itself is oxidation of an intermediate, the diradical or maleimide.

(9) Ebersson, L.; Barry, J. E.; Finkelstein, M.; Moore, W. M.; Ross, S. D. *Acta Chem Scand.*, in press.

(10) Skell, P. S.; Tenmak, R. L.; Seshadri, S. *J. Am. Chem. Soc.* **1983**, *105*, 5125 and previous work by this group. See also: Walling, C.; El-Taliawi, G. M.; Zhao, C. *Ibid.* **1983**, *105*, 5119.

We do not have an analytical method for S^- in our reaction mixtures that is completely reliable. We have tried to determine $[S^-]$ in runs in which $[S^-]_0$ was in excess both by ion chromatography and by a GC method in which methyl tosylate was added and S^- was determined as *N*-methylsuccinimide. The results from the two methods were not in good agreement, but both methods pointed to side reactions involving S^- . Since the succinimide polymer has both C-C and C-N linkages between succinimide groups, it must have some available N-H groups, which we might represent as PNH. The equilibrium shown in eq 12 now becomes possible. It is reasonable to expect



that PN^- is less effective than S^- in electron transfer. This proton transfer can, therefore, slow the $\text{SCl}-S^-$ reaction. Another possible path for consumption of S^- is Michael addition of S^- to maleimide and the anionic polymerization that such addition might initiate.⁹

Experimental Section

Chemicals. Reagent-grade *N*-chlorosuccinimide from the Aldrich Chemical Company was recrystallized from water-acetone and dried over P_2O_5 in vacuo before use; mp 149–151 °C (lit. mp 150–151 °C¹¹). The purity was assayed by an iodimetric procedure;¹² active chlorine was 26.4% corresponding to 99.6% purity. Tetra-*n*-butylammonium fluoborate was prepared as previously described.¹³ Linde ultrahigh purity nitrogen was used to remove oxygen and maintain an inert atmosphere during the electrochemical experiments. The nitrogen was saturated with acetonitrile (AN) before passage into the electrochemical cell. The purification of the AN, the preparation of *N*-methylsuccinimide, and the preparation of a standardized solution of tetra-*n*-butylammonium succinimide in AN were all carried out as described previously.¹

Apparatus and Instrumentation. Electrochemical experiments were performed using the following equipment supplied by EG&G Princeton Applied Research Corporation: a Model 175 universal programmer in conjunction with a Model 173 potentiostat/galvanostat and Model RE0089 X-Y recorder, jacketed cell bottom (K0064), cell top (K0066), purge tube (G0028), and glassy carbon electrode (G0021). Temperature control at 25 °C during electrochemical experiments was maintained with a Lauda Model C-3 circulator. For the experiments at 1 ± 1 °C an ice-

water bath was used. A tube (12-mm diameter \times 125-mm length) with a fritted glass tip (porosity "C") from Ace Glass (7209-06) was the anode compartment. A 50-mil Pt wire was inserted through a red rubber septum, and the septum was fitted over the end of the tube. The glass/septum boundary was wrapped with Parafilm M (American Can Company), and the air-tight seal prevented significant mixing of anolyte and catholyte solutions. A 2.3-mm diameter Pt disk sealed in soft glass and polished to a flat surface was employed for voltammetry. The working electrode for controlled-potential electrolyses was constructed from Pt gauze. Platinum electrodes were treated with chromic acid, rinsed with water, and dried before use. The Pt and glassy carbon voltammetric electrodes were manually polished between scans with γ -alumina (Gamal from Fisher Scientific Co.) on a felt polishing cloth. The reference electrode consisted of an Ag wire in contact with an AN solution containing 0.10 M AgNO_3 and 0.25 M TBAF, and it was terminated with a 3-mm diameter Vycor disk. For voltammetry experiments the reference electrode was placed into a salt bridge tube containing 0.25 M TBAF in AN, and it contacted the test solution through a Luggin capillary.

A Varian Model 2720, dual-column gas chromatograph equipped with a 6 ft \times 0.25 in. stainless steel column packed with 10% poly(*m*-phenyl ether) (PMPE) on 80/100-mesh Chromosorb W and a 6 ft \times 0.25 in. stainless steel column packed with Poropak Q was employed for product analyses. Infrared spectra were obtained with a Perkin-Elmer Model 281B infrared spectrophotometer.

Procedures. The general procedures for carrying out voltammetry and controlled-potential electrolyses of SCl were similar to those described previously.¹ Rate measurements of the $\text{SCl}-S^-$ reaction were made at 1 ± 1 °C with the cell bottom immersed in an ice-bath. A voltammetric scan at 200 mV s^{-1} of SCl in AN containing 0.25 M TBAF was initially executed. An aliquot of the standardized TBAS solution was added to the cell, the solution was mixed by magnetic stirring and N_2 deaeration for ca. 45 s, and then ca. 15 s were allowed for the solution to become quiescent before the first voltammetric sweep was made. The working electrode was removed from the cell between sweeps, polished, and replaced. Voltammetric sweeps were performed every 2–5 min to record the SCl concentration vs. time. The second-order rate constants were obtained from the appropriate linear plots of the experimental data.

Products from the SCl electrolyses and chemical reactions were analyzed without prior workup. Succinimide and *N*-methylsuccinimide were determined by GC using the PMPE column isothermally at temperatures of 180 and 160 °C, respectively. Chloride ion was determined as *n*-butyl chloride on Poropak Q at 200 °C using an on-column derivatization procedure.⁴ Determination of SH by IR was carried out differentially in 0.2-mm cells with AN as a reference. The intensity of the absorption at 3280 cm^{-1} (N-H stretch) was used as a measure of the SH concentration.

Registry No. SCl, 128-09-6; S^- , 28627-67-0.

(11) The Merck Index, 8th ed., Merck and Co., Inc.: Rahway, NJ, 1968; p 247.

(12) Waugh, T. D. "N-Bromosuccinimide, Its Reaction and Uses"; Arapahoe Chemicals, Inc., Boulder, CO, 1951; p 34.

(13) Rudd, E. J.; Finkelstein, M.; Ross, S. D. *J. Org. Chem.* 1972, 37, 1763.

A New Synthesis of Bicyclo[4.1.1]octa-2,4-diene and Its Cycloaddition Reactions with Dienophiles

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Bicyclo[4.1.1]octa-2,4-diene (**4**) has been synthesized by a new, nine-step route, starting from 2-[(trimethylsilyloxy)-1,3-butadiene and acrolein. Diene **4** proved almost as unreactive toward Diels-Alder cycloadditions as the previously studied 7,7-dimethyl derivative **1**. However, unlike **1**, **4** did react with phenyltriazolinedione to give a **4** + 2 cycloadduct. This difference between **1** and **4** is discussed in terms of a steric effect involving the endo methyl group in **1**, an explanation that is supported by the results of molecular mechanics calculations.

Several years ago we reported the synthesis of 7,7-dimethylbicyclo[4.1.1]octa-2,4-diene (**1**).¹ As part of our

exploration of the chemistry of **1**,^{2,3} we investigated its Diels-Alder reactivity.⁴ The diene proved quite inert