Reactions of Nitrosonium Ethyl Sulfate with Olefins and Dienes: An Experimental and Theoretical Study

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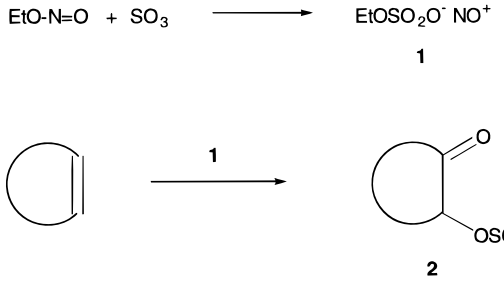
Nitrosonium ethyl sulfate (**1**), which is generated in situ from ethyl nitrite and sulfur trioxide, is a convenient reagent for the one-pot transformation of olefins and dienes into substituted aldehydes and ketones. New experimental and theoretical aspects of this reaction are discussed. A DFT and ab initio computational study is undertaken to provide further insight into the mechanism of electrophilic nitrosation, including the initial π-complexes, transition states, and the intermediates involved in subsequent carbonyl formation.

Electrophilic addition across olefinic double bonds is a fundamental process in organic chemistry that has both theoretical value and far-reaching synthetic applications. Indisputably, the Ad_E reaction of olefins constitutes a versatile and reliable method for their functionalization, making the search for new electrophilic reagents, as well as the development of methods to enhance the reactivity of weak electrophiles, an important task.[1−3]

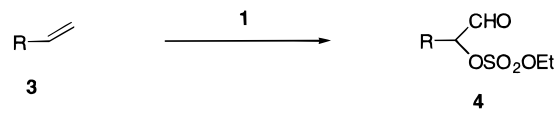
In recent years, we have proposed a number of new electrophilic reagents based on the novel concept involving activation of weak electrophiles with sulfur trioxide.[4] In a previous paper[5] we reported the application of this concept to the electrophilic addition of ethyl nitrite to *cycloalkenes*. This paper contributes an important synthetic development of this idea augmented with density functional theory (DFT) and ab initio theoretical studies to better understand the mechanism of nitrosation.

Results and Discussion

Earlier we found[5] that ethyl nitrite reacts instantly with an equimolar amount of SO_3 at −50 to −30 °C in CH_2Cl_2 to give a highly reactive nitrosating reagent, nitrosonium ethyl sulfate (**1**), which was used in situ without purification or isolation. Reagent **1** reacts with cyclic olefins to form α-ethylsulfato cycloalkanones **2** in good yields.



As a development of this idea we now report the results of our experimental and theoretical studies on the reactions of **1** with terminal olefins and dienes. In the case of 1-hexene (**3a**), 1-heptene (**3b**), and 1-octene (**3c**) the reaction furnished the corresponding α-ethylsulfato-substituted aldehydes **4a**−**c** in good yields (70−75%).



R = (a) C_4H_9; (b) C_5H_{11}; (c) C_6H_{13}

The reactions proceed regiospecifically in accordance with the Markovnikov rule. It should be emphasized that the above reaction of **1** is a rare case of direct conversion of the terminal olefinic carbon into the aldehyde group.

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(4) (a) For a review, see: Zefirov, N. S. In *Organic Synthesis: Modern Trends*, Proceedings of the 6th IUPAC Symposium on Organic Synthesis, Moscow, 1986; Chizhov, O. S., Ed.; Blackwell: Oxford, UK, 1987, p 122. (b) SO_3 + RSCl: Zefirov, N. S.; Kos'min, A. S.; Sorokin, V. D.; Shastin, A. V.; Balenkova, E. S. *Dokl. Akad. Nauk SSSR*, **1984**, *276*, 1139. (c) $SO_3 + Cl_2$: Zefirov, N. S.; Kos'min, A. S.; Sorokin, V. D.; Zhdankin, V. V. *J. Org. Chem.* **1984**, *49*, 4086. (d) SO_3 + AcF: Krespan, C. G.; England, D. C. *J. Org. Chem.* **1975**, *40*, 2937. Shastin, A. V.; Gavrishova, T. N.; Balenkova, E. S. *Zh. Org. Khim.* **1985**, *21*, 1862. Gavrishova, T. N.; Shastin, A. V.; Balenkova, E. S. *Zh. Org. Khim.* **1991**, *27*, 673. (e) $SO_3 + R_2NCl$: Zefirov, N. S.; Zyk, N. V.; Kolbasenko, S. I.; Kutateladze, A. G. *Sulfur Lett.* **1984**, *2*, 95. Zefirov, N. S.; Zyk, N. V.; Kolbasenko, S. I.; Kutateladze, A. G. *J. Org. Chem.* **1985**, *50*, 4539. (f) $SO_3 + XeF_2$: Brel', V. K.; Gakh, A. A.; Zhdankin, V. V.; Zefirov, N. S.; Koz'min, A. S.; Korkin, A. A.; Kutateladze T. G.; Caple, R.; Lermontov, S. A.; Plokhikh, I. G.; Safronov, S. O.; Stang, P. J.; Chovnikova, N. G. *Dokl. Akad. Nauk SSSR* **1990**, *313*, 1131. (g) SO_3 + RSSR′: Kutateladze, A. G.; Zefirov, N. S.; Zyk, N. V. *Sulfur Rep.* **1992**, *11*, 233. (h) $SO_3 + RSNR_2'$: Zefirov, N. S.; Zyk, N. V.; Kutateladze, A. G.; Lapin, Yu. A. *Zh. Org. Khim.* **1987**, *23*, 392. Zyk, N. V.; Kolbasenko, S. I.; Kutateladze A. G.; Lapin, Yu. A. *Zh. Org. Khim.* **1988**, *24*, 1209. (i) SO_3 + RSOR′: Zefirov, N. S.; Zyk, N. V.; Lapin, Yu. A.; Kutateladze, A. G.; Ugrak, B. I. *Zh. Org. Khim.* **1992**, *28*, 1226. (j) $SO_3 + R_2N{-}S{-}NR_2$: Zefirov, N. S.; Zyk, N. V.; Kutateladze, A. G.; Lapin, Yu. A. *Zh. Org. Khim.* **1987**, *23*, 229. Zefirov, N. S.; Zyk, N. V.; Kutateladze, A. G.; Potekhin, K. A.; Struchkov, Yu. T. *Sulfur Lett.* **1987**, *6*, 139. (k) $SO_3 + RONO_2$: Zefirov, N. S.; Zyk, N. V.; Lapin, Yu. A.; Kutateladze, A. G. *Sulfur Lett.* **1988**, *8*, 143. Zyk, N. V.; Lapin, Yu. A.; Kutateladze, A. G.; Zefirov, N. S. *Zh. Org. Khim.* **1988**, *24*, 889. (l) $SO_3 + R_2NSCl$: Kutateladze, A. G.; Zyk, N. V.; Denisko, O. V.; Zefirov, N. S. *Zh. Org. Khim.* **1991**, *27*, 659.

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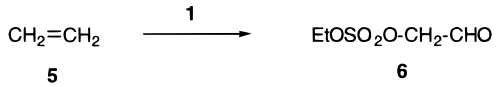
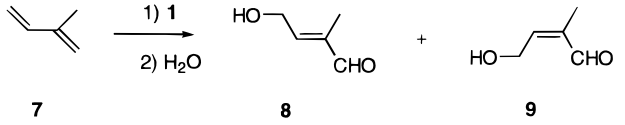
Parent ethylene (**5**) also reacted with reagent **1**; passing gaseous ethylene through freshly prepared **1** in CH_2Cl_2 at −40 °C yielded the ethyl sulfate of glycolaldehyde (**6**) (40%).

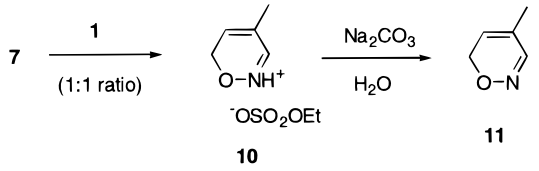


An interesting result was obtained for a simple conjugated diene, isoprene (**7**), which is one of the most important industrial dienes, as well as the main building block of many naturally occurring molecules. Reaction of **1** with isoprene at −55 °C followed by a slow warming to room temperature and a subsequent aqueous workup resulted in a single product, 4-hydroxyaldehyde **8** (78%), with E-configuration of the C=C double bond.[6]



However, a small variation in the reaction conditions led to a dramatically different result. When aqueous ethanol was added to the reaction mixture at −55 °C prior to increasing the temperature, a mixture of two stereoisomeric 4-hydroxyaldehydes **8** and **9** is obtained in the ratio of 1:6.5,[7] (42%). That is, the Z-isomer **9** is now the major product.

In both cases we used a 2:1 ratio of reagent **1** to isoprene in accordance with our previous observations.[5] However, in the case of equimolar amounts of **1** and isoprene (the conditions of "the primary adduct stage", see ref 5), 4-methyl-1,2,6*H*-oxazinium ethyl sulfate (**10**) was obtained as the only product.



The subsequent treatment of the salt **10** with an aqueous solution of sodium carbonate furnished oxazine **11** as a free base (44%).

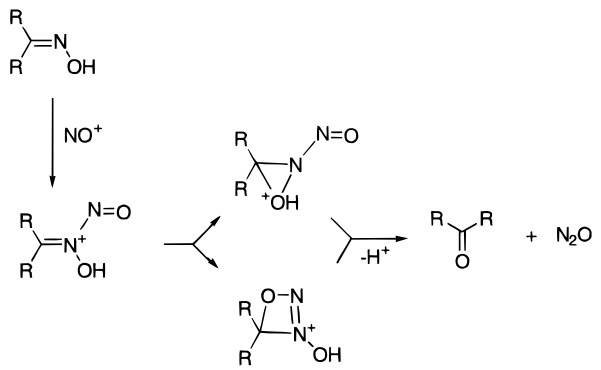
To gain mechanistic insight we conducted a DFT study on the species potentially involved in this reaction sequence. Not unexpectedly, we were unable to locate a σ-complex on the energy hypersurface. It was found that the most stable initial species of the electrophilic attack is a *s-cis* π-complex ***Ia***, which is about 1 kcal/mol more stable than *s-trans* π-complex ***IIa*** (Table 1). The fact that a "classical" σ-complex is much less stable than the π-complex is certainly not unprecedented in olefin nitrosation. Raghavachari et al.[8] showed that, for example, in ethylene nitrosation the π-complex (CH_2CH_2/NO^+) is about 14 kcal/mol more stable than the σ-complex ($ON-CH_2CH_2^+$) at CCDST(4)/6-31G(d) and MP4/6-31G(d) levels of theory. At the same time we find that the dihydrooxazinium cation ***IIIa*** (a boat conformation) lies only 4.2 kcal/mol (B3LYP/6-31G(d) or 11.8 at MP2/6-311G(d)) above the *s-cis* π-complex ***Ia***, which makes it easily accessible at the reaction temperatures.

Summarizing our experimental and theoretical evidence, we can therefore offer the following mechanistic rationale for the process. Despite somewhat contradicting views on the mechanism of olefin nitrosation,[9] there is little doubt that the reaction with isoprene begins with an electrophilic attack of the nitrosonium cation (NO^+). Our computational data seem to suggest that the *s-cis* π-complex ***Ia*** (which is in equilibrium with dihydrooxazinium cation ***IIIa***) is formed as an initial product of such electrophilic attack, followed by deprotonation to form oxazine **11** (or its salt **10**). In the case when an equimolar amount of the nitrosating reagent is used, a basic workup of the reaction mixture then furnishes oxazine as the only product.[10]

If a 2-fold excess of the nitrosating reagent is used, *N*-nitrosooxazinium is formed, which in turn can be quenched at low temperatures by a water/alcohol mixture and hydrolyzed into the Z-hydroxyaldehyde **9** (Path A, Scheme 1). Alternatively, in the absence of water it can ring-open to form *N*-nitrosoaldoxime (**B**−**Z**), which upon warming to room temperature (prior to aqueous workup) has a chance to equilibrate with (**B**−**E**).

We ran DFT calculations (B3LYP/6-31G*) for isomers **8** and **9** and found the E-isomer **8** to be approximately 2.4 kcal/mol more stable than the Z-isomer **9**. Self-consistent reaction field computations to account for solvent effects (self-consistent isodensity polarized continuum model, SCIPCM) showed the same energy difference for the two isomers.

The transformation of the nitroso group in the initial products of electrophilic addition into a carbonyl is known to occur via nitrosooxime tautomerization with subsequent hydrolysis of the oxime into the free carbonyl. Such hydrolyses are facilitated by NO^+ when excess nitrosating species are present. This reaction, however, has been a point of controversy in the literature. In a mechanistic study of a ketoxime reacting with ^{18}O-enriched nitrous acid, Wieland and Grimm considered two possible mechanisms:



On the basis of a 89% enrichment of nitrous oxide ($N_2-^{18}O$) they ruled out the four-membered intermediate, concluding that the reaction involves an intermediate formation of *N*-nitrosooxaziridine.[11] Kliegman and Bar-

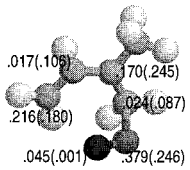
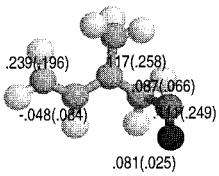
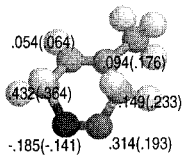
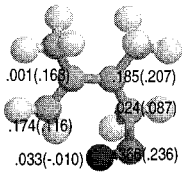
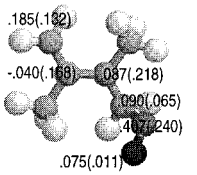
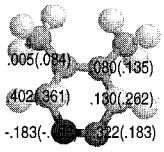
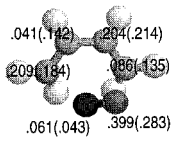
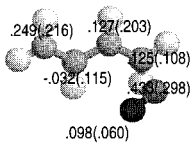
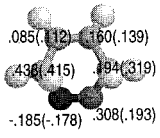
(6) *E*-configuration of the double bond in **8** was determined by a NOE experiment.

(7) Determined from the integral intensities of corresponding peaks in the ^1H NMR spectrum.

(8) Raghavachari, K.; Reents, W. D., Jr.; Haddon, R. C. *J. Comput. Chem.* **1986**, *7*, 265−73.

(9) (a) Kadzjauskas, P. P.; Zefirov, N. S. *Usp. Khim.* **1968**, *37*, 1243. (b) Ingold, C. K. *Structure and mechanism in organic chemistry*; Cornell University Press: Ithaca, NY, 1953. (c) Meinwald, J.; Meinwald, Y. C.; Baker, T. N. *J. Am. Chem. Soc.* **1963**, *85*, 2513.

Table 1. NO^+ Addition to Isoprene, Dimethylbutadiene, and Butadiene; DFT and ab Initio Results[a,b]

isoprene			
	Ia	***IIa***	***IIIa***
	s-cis π-complex	*s-trans π-complex*	*oxazinium*
E_{REL} *(kcal/mol)*	**0.0 (0.0)**	**1.2 (1.1)**	**11.8 (4.2)**
[C-N], Å	2.235 (1.901)	2.341 (1.938)	1.466 (1.462)
[N-O], Å	1.130 (1.141)	1.128 (1.137)	1.228 (1.232)
[C-O], Å	2.609 (2.792)	-	1.558 (1.569)
2,3-dimethyl-butadiene			
	Ib	***IIb***	***IIIb***
	s-cis π-complex	*s-trans π-complex*	*oxazimium*
E_{REL} *(kcal/mol)*	**0.0 (0.0)**	**2.0 (2.5)**	**10.4 (2.7)**
[C-N], Å	2.237 (1.880)	2.359 (1.907)	1.457 (1.430)
[N-O], Å	1.133 (1.144)	1.131 (1.140)	1.231 (1.241)
[C-O], Å	2.521 (2.714)	-	1.543 (1.536)
butadiene			
	Ic	***IIc***	***IIIc***
	s-cis π-complex	*s-trans π-complex*	*oxazinium*
E_{REL} *(kcal/mol)*	**0.1 (1.3)**	**0.0 (0.0)**	**14.0 (3.8)**
[C-N], Å	2.288 (2.044)	2.410 (2.075)	1.470 (1.438)
[N-O], Å	1.129 (1.130)	1.127 (1.126)	1.226 (1.238)
[C-O], Å	2.562 (2.755)	-	1.557 (1.543)

[a] MP2/6-311G(d) values (B3LYP/6-31G(d) values are in parenthesis). The DFT energies are ZPE-corrected. MP2 energies are ZPE-corrected only for butadiene derivatives ***Ic-IIIc***. [b] Structures are displaying the Mulliken charges (with hydrogen charges summed into the heavy atoms). Methyl charges are omitted

nes later revised Wieland's results, contending that there is no need to invoke the three-membered ring intermediate as the mechanism can simply be envisioned as a hydrolysis of the *N*-nitrosooxime.[12] They, however, revived the oxadiazacyclobutene intermediate to explain partial N_2 formation in this reaction.

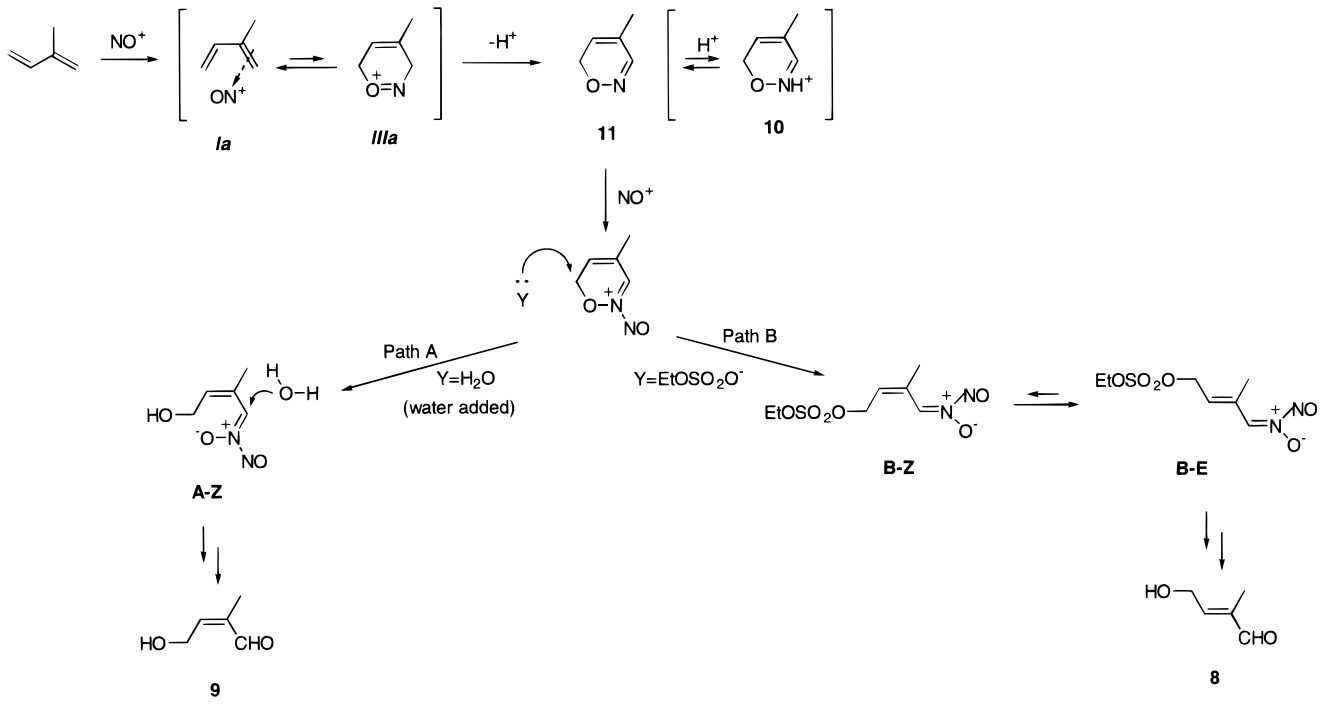
We explored this transformation theoretically and carried out both DFT and high level ab initio studies of the species potentially involved in the rearrangement. First, we optimized molecular geometries of *syn*- and *anti*-*N*-nitrosoformaldoximes (deprotonated in Table 2 and protonated in Table 3) at B3LYP/6-31G(d) and MP2/6-311G(d) levels of theory. We then optimized the geometries of the three- and four-membered ring intermediates and located the respective transition states leading to these intermediates. We also located the transition states for the N_2O extrusion regenerating the free carbonyl. All of these computations were accompanied by vibrational analyses. No imaginary frequencies were observed for the intermediates, and all of the calculated transition states had one imaginary frequency corresponding to the expected normal mode associated with the reaction coordinate. We also ran higher level single point MP4/6-311+G(d) computations for the MP2/6-311G(d) geometries. Additionally, we estimated the impact of the solvent by employing the self-consistent reaction field computations at the MP4/6-311+G(d) level in conjunction with SCIPCM for all of the species involved, including the transition states in the deprotonated series. Our findings seem to indicate that the barriers for the formation of the three- and four-membered intermediates, about 50 kcal/mol, are too high to be accessible for the molecules even at room temperature (see Tables 2

(10) Such process is certainly not unprecedented in the literature; as early as three decades ago oxazine **11** was synthesized by the reaction of nitrosonium hydrosulfate $NOHSO_4$ with isoprene: Klamann, D.; Fligge, M.; Weyerstahl, P.; Kratzer, J. *Chem. Ber.* **1966**, *99*, 556.

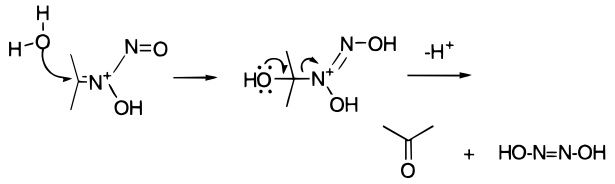
(11) Wieland, T.; Grimm, D. *Chem. Ber.* **1963**, *96*, 275.

(12) Kliegman, J. M.; Barnes, R. K. *J. Org. Chem.* **1972**, *37*, 4223.

Scheme 1

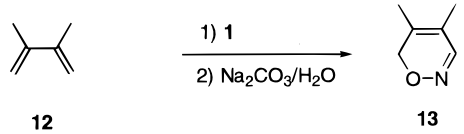


and 3). We therefore contend that a simple hydrolysis of *N*-nitrosooximes is the most likely channel for NO^+-assisted transformation of oximes. Subsequent degradation of the initial inorganic product of such hydrolysis, hyponitrous acid, could conceivably account not only for the formation of N_2O but also for the formation of the other two components of the gaseous mixture, N_2 and NO:



In summary, with minor variations in the reaction conditions, nitrosation of isoprene **7** with nitrosonium ethyl sulfate **1** can be directed to afford at least three products with surprisingly good selectivity. One of them, E-aldehyde **8**, is an important starting material for syntheses of various isoprenoid compounds.[13] It should also be noted that the regiochemistry of this isoprene nitrosation is exclusively Markovnikov, in keeping with the results of **1** reacting with olefins **3a**−**c**.

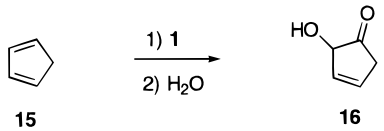
Despite our multiple efforts to obtain 4-hydroxyaldehydes (of type **8** and **9**) only 4,5-dimethyl-1,2,6*H*-oxazine (**13**) was obtained in a quantitative yield (97%) as a result of the nitrosation of 2,3-dimethyl-1,3-butadiene (**12**).



The DFT study of the 2,3-dimethylbutadiene nitrosation again showed that the most stable initial species in this reaction is the *s-cis* π-complex (***Ib***) (Table 1), just as in the reaction with isoprene. It is 2.47 kcal/mol below its *s-trans* isomer (***IIb***). The π-complexes are in equilibrium with the oxazinium (***IIIb***), which lies only 2.7 (10.4 MP2) kcal/mol above the *s-cis* isomer. Conceivably, the introduction of the second methyl group simply prevents the oxazinium ring from opening under a nucleophilic attack by either water or ethyl sulfate anion. As a result of such steric hindrance the oxazinium cation (***IIIb***) then has only one channel for stabilization, deprotonation, which furnishes the oxazine **13**.

Finally, the reaction of **1** with 1,3-butadiene (**14**) did not produce any monomeric product but rather yielded a mixture of oligomeric products, which showed the presence of formyl and hydroxy groups by IR spectroscopy. Computationally, one difference was that both B3LYP/6-31G(d) and MP2/6-311G(d) computations in this case showed a slight energy preference for the *s-trans* π-complex ***IIc*** (Table 1). It is plausible that such an acyclic intermediate would be much more prone to polymerization. The absence of methyl substitution may also allow for secondary nitrosation of the double bond being formed between atoms 2 and 3 in the initial 1,4-adduct.

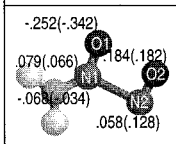
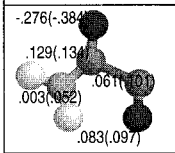
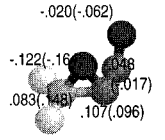
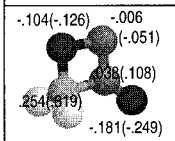
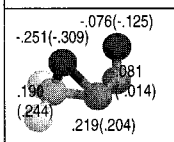
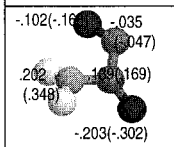
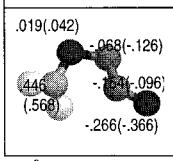
Cyclopentadiene (**15**), a widely used 1,3-diene with rigidly fixed *s-cis* arrangement of double bonds, yields only a single product, 2-hydroxycyclopent-3-enone (**16**)[14] (55%), when reacted with **1**.



Ketone **16** is the result of the Markovnikov 1,2-addition of **1** to one of the double bonds. Thus, the reaction proceeds differently in comparison to acyclic dienes where

(13) Pattenden, G.; Way, G. E.; Weedon, B. C. L. *J. Chem. Soc., C* **1970**, 235. Pommer, H.; Nürrenbach, A. *Pure Appl. Chem.* **1975**, *43*, 527; Wehrli, P. A., Schaer, B. *Synthesis* **1977**, 649.

Table 2. Relative Energies,[a] Charges,[b] and Bond Lengths in *IVa*−*XIa*

Compound/TS	Name/Theory level	Bond length, (Å)						E_{REL} kcal/mol
		C-N1	N1-O1	C-O1	N1-N2	N2-O2	C-O2	
	***Syn*-N-nitrosoformaldoxime (deprot) (IVa)**							
	B3LYP/6-31G(d)	1.296	1.226	-	1.742	1.158	-	0.0
	MP2/6-311G(d)	1.302	1.219	-	2.075	1.162	-	0.0
	MP4/G-311+G(d)// MP2/6-311G(d)							0.0
	MP4/G-311+G(d)// MP2/6-311G(d) SCIPCM							0.0
	***Anti*-N-nitrosoformaldoxime (deprot) (Va)**							
	B3LYP/6-31G(d)	1.293	1.229	-	1.768	1.162	-	6.2
	MP2/6-311G(d)	1.308	1.210	-	1.935	1.160	-	8.3
	MP4/G-311+G(d)// MP2/6-311G(d)							6.5
	MP4/G-311+G(d)// MP2/6-311G(d) SCIPCM							5.2
	***N*-nitroso oxaziridine (VIa)**							
	B3LYP/6-31G(d)	1.435	1.464	1.411	1.462	1.192	-	13.9
	MP2/6-311G(d)	1.436	1.470	1.408	1.477	1.194	-	18.2
	MP4/G-311+G(d)// MP2/6-311G(d)							19.8
	MP4/G-311+G(d)// MP2/6-311G(d) SCIPCM							17.4
	***Oxadiazacyclobutene N-oxide (VIIa)***							
	B3LYP/6-31G(d)	1.484	1.228	-	1.298	1.450	1.430	7.0
	MP2/6-311G(d)	1.471	1.223	-	1.328	1.436	1.430	11.1
	MP4/G-311+G(d)// MP2/6-311G(d)							12.1
	MP4/G-311+G(d)// MP2/6-311G(d) SCIPCM							7.3
	***TS (VIIIa)** leading to oxaziridine VIa*							
	B3LYP/6-31G(d)	1.361	1.328	1.928	1.575	1.176	-	48.8
	MP2/6-311G(d)	1.362	1.363	1.813	2.176	1.154	-	50.8
	MP4/G-311+G(d)// MP2/6-311G(d)							49.8
	MP4/G-311+G(d)// MP2/6-311G(d) SCIPCM							49.0
	***TS (IXa):** N_2O extrusion from VIa*							
	B3LYP/6-31G(d)	1.538	1.800	1.327	1.283	1.205	-	21.8
	MP2/6-311G(d)	1.530	1.856	1.332	1.266	1.209	-	30.7
	MP4/G-311+G(d)// MP2/6-311G(d)							28.9
	MP4/G-311+G(d)// MP2/6-311G(d) SCIPCM							26.5
	***TS (Xa)** leading to VIIa*							
	B3LYP/6-31G(d)	1.406	1.246	-	1.359	1.280	2.002	46.5
	MP2/6-311G(d)	1.432	1.207	-	1.419	1.296	1.985	51.6
	MP4/G-311+G(d)// MP2/6-311G(d)							51.2
	MP4/G-311+G(d)// MP2/6-311G(d) SCIPCM							48.9
	***TS (XIa):** N_2O extrusion from VIIa*							
	B3LYP/6-31G(d)	2.222	1.213	-	1.336	1.411	1.300	28.7
	MP2/6-311G(d)	2.577	1.257	-	1.268	1.645	1.234	44.5
	MP4/G-311+G(d)// MP2/6-311G(d)							40.8
	MP4/G-311+G(d)// MP2/6-311G(d) SCIPCM							29.4

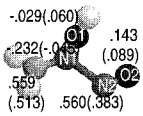
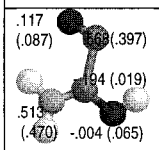
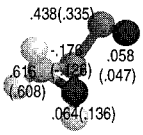
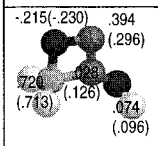
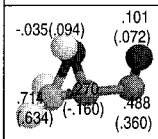
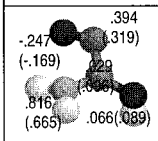
[a] The DFT and MP2 energies are ZPE-corrected. [b] Structures are displaying the Mulliken charges obtained at MP4/G-311+G(d)// MP2/6-311G(d) level of theory with MP4/6-311+G(d)// MP2/6-311G(d) SCIPCM charges in parenthesis (hydrogen charges summed into the heavy atoms)

the products of 1,4-addition were exclusively formed. Our DFT study revealed that the π-complex ***XII*** is again by far the most stable initial species. In fact, we were unable to optimize the geometry of an oxazinium-like intermediate without imposing certain geometry constraints. Such unconstrained computations, starting with a bicyclo-[2.2.1] structure similar to ***XIII***, would inevitably revert to the π-complex ***XII***. Only when we constrained the C−N and C−O bond lengths to that of the respective bond length values in oxazinium ***IIIa*** were we able to optimize the geometry at B3LYP/6-31G(d) level. Surprisingly, the vibrational analysis showed no imaginary frequencies, which would imply that the bicyclic structure ***XIII*** is a very shallow minimum with an insignificantly low barrier leading to the π-complex ***XII***. The energy of ***XIII*** is still about 20.3 kcal/mol above the π-complex (see Table 4, compare with 2.7−4.2 kcal/mol at this level of theory for the oxaziniums ***IIIa*−*c***, Table 1). We therefore conclude that the absence of the isomeric product, 3-hydroxycyclopent-4-enone, is due to high skeletal strain in ***XIII*** compared with acyclic dienes.

Reaction of **1** with 1,5-cyclooctadiene (**17**) afforded

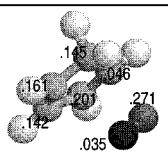
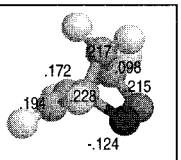
(14) The structural assignment of **24** was based on the presence of the intramolecular H-bond in the IR experiment and the absence of spin−spin coupling constant ^3J for H_2C and HCO protons in the ^1H NMR experiment.

Table 3. Relative Energies,[a] Charges,[b] and Bond Lengths in *IVb−VIIIb and Xb*

Compound/TS	Name/Theory level	Bond lengths, (Å)						E_{REL}, kcal/mol
		C-N1	N1-O1	C-O1	N1-N2	N2-O2	C-O2	
	***Syn-N-nitrosoformaldoxime (IVb)***							
	B3LYP/6-31G(d)	1.274	1.360	-	1.945	1.116	-	**0.0**
	MP2/6-311G(d)	1.279	1.375	-	2.054	1.114	-	**0.0**
	***Anti-N-nitrosoformaldoxime (Vb)***							
	B3LYP/6-31G(d)	1.271	1.348	-	1.945	1.116	-	**1.6**
	MP2/6-311G(d)	1.277	1.348	-	2.043	1.115	-	**2.5**
	***N-nitroso oxaziridine (protonated) (VIb)***							
	B3LYP/6-31G(d)	1.421	1.567	1.492	1.856	1.128	-	**43.1**
	MP2/6-311G(d)	1.420	1.532	1.491	1.912	1.131	-	**46.6**
	***Oxadiazacyclobutene N-hydroxy (VIIb)***							
	B3LYP/6-31G(d)	1.480	1.332	-	1.276	1.351	1.459	**24.9**
	MP2/6-311G(d)	1.473	1.321	-	1.285	1.343	1.448	**35.0**
	***TS (VIIIb)*** *leading to oxaziridine VIb*							
	B3LYP/6-31G(d)	1.370	1.493	1.811	1.911	1.122	-	**53.1**
	MP2/6-311G(d)	1.361	1.498	1.792	2.001	1.125	-	**58.1**
	***TS (Xb)*** *leading to VIIb*							
	B3LYP/6-31G(d)	1.389	1.341	-	1.339	1.246	2.009	**55.9**
	MP2/6-311G(d)	1.375	1.332	-	1.340	1.263	1.961	**69.3**

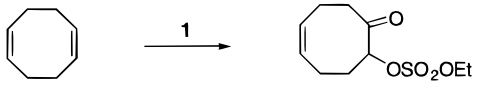
[a]The DFT and MP2 energies are ZPE-corrected. [b]Structures are displaying the Mulliken charges obtained at MP2/6-311G(d) level of theory with B3LYP/6-31g* charges in parentheses (hydrogen charges summed into the heavy atoms)

Table 4. B3LYP/6-31G(d) Relative Energies,[a] Charges,[b] and Bond Lengths in *XII* and *XIII*

	 ***XII***	 ***XIII***
E_{REL} (kcal/mol)	**0.0**	**20.3**
[C-N], Å	2.056	1.460
[N-O], Å	1.132	1.240
[C-O], Å	2.744	1.570

[a] with ZPE correction; [b] Mulliken charges with hydrogen charges summed into the heavy atoms.

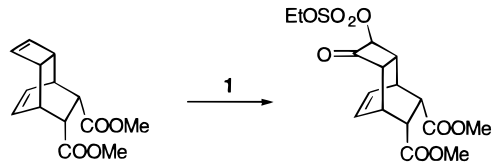
exclusively the ethylsulfato ketone **18** (74%).



17 **18**

Transannular ring closure to give bicyclo[3.3.0]octane derivatives or hydride shifts, which commonly accompany the additions of "effectively strong electrophiles" (for definition see ref 15) to this diene,[16] are not observed in this case.

Predictably, **1** reacted with the more active (cyclobutene) double bond of diene **19**, yielding the product of 1,2-addition (**20**, 76%). As in the previous case, we did not observe the formation of the transannular cross-cyclization products, which are typical for electrophilic additions to this diene.[17]



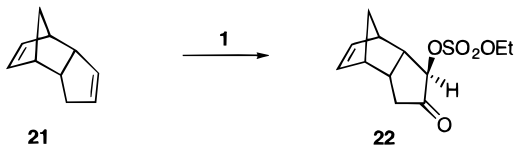
19 **20**

Dicyclopentadiene (**21**) adds the reagent **1** exclusively to the less strained double bond to yield ethylsulfato ketone **22** (82%).

(15) (a) See ref 2a. (b) Zefirov, N. S.; Bodrikov, I. V. *Zh. Org. Khim.* **1983**, *19*, 225. (c) See also ref 15 in: Zefirov, N. S.; Zyk, N. V.; Borisenko, A. A.; Krysin, M. Yu.; Schestakova, T. G. *Tetrahedron* **1983**, *39*, 3145.

(16) Zefirov, N. S.; Sadovaja, N. K.; Novgorodtseva, L. A.; Bodrikov, I. V. *Zh. Org. Khim.* **1978**, *14*, 1806.

(17) Kondo, A.; Yamane, T.; Ashida, T.; Sasaki, T.; Kanematsu, K. *J. Org. Chem.* **1978**, *43*, 1180. Zefirov, N. S.; Koz'min, A. S.; Kirin, V. N.; Zhdankin, V. V.; Caple, R. *J. Org. Chem.* **1981**, *46*, 5264.



21 22

In conclusion, we have developed a new one-pot transformation for terminal olefins and dienes into α-substituted aldehydes and internal olefins into the corresponding ketones. The studied reaction can be considered a versatile technique for olefin functionalization, affording valuable synthetic intermediates. The common feature of the mechanism is that, unlike a typical electrophilic addition, the nitrosation reaction seems to proceed via a π-complex, not a σ-intermediate. Insignificant development of carbocationic character in such π-complexes could then explain the known "reluctance" of nitrosation reactions to undergo skeletal rearrangements.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$. All reactions were followed by TLC with precoated aluminum TLC plates (silica gel, Silufol, Czech Republic). Preparative column chromatography involved silica gel (Silpearl) and ethyl acetate−hexane mixtures as eluent. All solvents and reagents were additionally purified and dried by standard techniques. Ethyl nitrite was synthesized as previously reported.[18] SO_3 was obtained from 60% oleum. Freshly distilled SO_3 was used, which was weighed and dissolved in CH_2Cl_2.

Computations. Ab initio and DFT computations were performed on a dual mips R10000 processor SGI Octane workstation equipped with 1GB memory using Gaussian 94 Revision E.2 computational package.[19] The input geometries were created and preoptimized using a force field geometry optimization as implemented in Chem3D (Cambridgesoft). Full geometry optimizations were then performed at B3LYP/6-31G(d) and MP2/6-311G(d) levels of theory. Single point computations at the MP4/6-311G(d) level of theory were performed for the series of nitrosoformaldoximes (Table 2). Self-consistent reaction field (SCRF) computations were then performed to account for solvent polarity effects utilizing SCIPCM. These also were run as single point calculations without further geometry optimization, MP4-SCIPCM/6-311G(d)//MP2/6-311G(d) (Table 2).

General Procedure for the Addition Reaction. A three-neck flask fitted with an addition funnel, stirrer, and argon inlet was charged with a solution of SO_3 in CH_2Cl_2. The mixture was cooled to −50 °C, and a solution of EtONO in CH_2Cl_2 was added dropwise while the temperature was maintained at −50 to −30 °C. The resulting mixture was stirred for 0.5 h at this temperature, and a solution of olefin in CH_2Cl_2 was added dropwise at −50 to −30 °C. Further workup involved 1 h of stirring at −50 °C, after which the temperature was allowed to rise slowly to room temperature. After treatment with cold water, extraction with $CHCl_3$, and drying over $MgSO_4$, the solvent was evaporated in vacuo. Crude product was chromatographed.

Reaction of 1-Hexene (3a). From 0.95 g (11.9 mmol) of SO_3 in 20 mL of CH_2Cl_2, 1.78 g (23.7 mmol) of EtONO in 16 mL of CH_2Cl_2, and 0.4 g (4.8 mmol) of **3a** in 20 mL of CH_2Cl_2 was obtained 0.75 g (70%) of ethyl sulfate of 2-hydroxyhexanal (**4a**) (eluent hexane/AcOEt/$CHCl_3$ = 1:3:3; colorless oil, R_f 0.16): IR 1760, 1400, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.91 (narrow t, 3H), 1.20−1.55 (m, 4H), 1.43 (t, 3H, J = 7.1 Hz), 1.87 (m, 2H), 4.45 (m, 2H), 4.83 (dd, 1H, J = 7.0, 5.5 Hz), 9.64 (s, 1H). Anal. Calcd for $C_8H_{16}O_5S$: C, 42.84; H, 7.19. Found: C, 42.75; H, 7.19.

Reaction of 1-Heptene (3b). From 1.28 g (16.0 mmol) of SO_3 in 25 mL of CH_2Cl_2, 1.64 g (22.0 mmol) of EtONO in 20 mL of CH_2Cl_2, and 0.71 g (7.2 mmol) of **3b** in 20 mL of CH_2Cl_2 was obtained 1.29 g (75%) of ethyl sulfate of 2-hydroxyheptanal (**4b**) (eluent hexane/AcOEt = 3:1; colorless oil, R_f 0.23): IR 1740, 1400, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9 (narrow t, 3H), 1.20−1.50 (m, 6H), 1.4 (t, 3H, J = 7.1 Hz), 1.7−2.0 (m, 2H), 4.4 (m, 2H), 4.78 (dd, 1H, J = 7.7, 5.6 Hz), 9.6 (s, 1H); ^{13}C NMR δ 13.8, 14.4, 22.1, 23.8, 29.5, 31.0, 70.1, 85.5, 196.1. Anal. Calcd for $C_9H_{18}O_5S$: C, 45.36; H, 7.61. Found: C, 45.54; H, 7.63.

Reaction of 1-Octene (3c). From 1.67 g (21.0 mmol) of SO_3 in 30 mL of CH_2Cl_2, 2.13 g (28.4 mmol) of EtONO in 25 mL of CH_2Cl_2, and 1.06 g (9.5 mmol) of **3c** in 25 mL of CH_2Cl_2 was obtained, 1.67 g (70%) of ethyl sulfate of 2-hydroxyoctanal (**4c**) (eluent heptane/AcOEt = 3:1; colorless oil, R_f 0.24): IR 1740, 1400, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9 (narrow t, 3H), 1.1−2.1 (group of m, 13H), 4.3 (m, 2H), 4.7 (m, 1H), 9.5 (s, 1H). Anal. Calcd for $C_{10}H_{20}O_5S$: C, 47.60; H, 7.99. Found: C, 47.48; H, 7.89.

Reaction of Ethylene (5). To a solution of 1.27 g (16.0 mmol) of SO_3 in 25 mL of CH_2Cl_2 was added the solution of 2.38 g (32.0 mmol) of EtONO in 20 mL of CH_2Cl_2 dropwise while the temperature was maintained at −55 °C. After 0.5 h of stirring at this temperature, gaseous ethylene was passed through the reaction mixture for 2 h. Further treatment was performed according to the general procedure and gave 0.45 g (40%, based on SO_3) of ethyl sulfate of glycolaldehyde (**6**) (eluent hexane/AcOEt = 2:1; yellowish oil, R_f 0.15): IR 1720, 1380, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.4 (t, 3H, J = 7.1), 4.0−4.9 (m, 4H), 9.3 (s, 1H).

Reaction of Isoprene (7). (a) In Conditions of Kinetic Control. To a solution of 1.3 g (16.3 mmol) of SO_3 in 30 mL of CH_2Cl_2 was added the solution of 2.65 g (35.3 mmol) of EtONO in 25 mL of CH_2Cl_2 dropwise while the temperature was maintained at −55 °C. After 0.5 h of stirring at this temperature, the solution of 0.48 g (7.1 mmol) of **7** in 18 mL of CH_2Cl_2 was added dropwise. After 1 h of stirring at −55 °C, the 1:1 water−ethanol mixture (20 mL) was added as quickly as possible. Further treatment was performed according to the general procedure. As a result, 0.3 g (42%) of a mixture of *Z*- and *E*-isomers of 4-hydroxy-2-methylbut-2-enal (**9** and **8**)[20] was obtained (eluent hexane/AcOEt = 3:1; colorless oil, R_f 0.32): IR 3600−3200, 1690, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.85 (q, 3H of **8**, J = 7.0 Hz), 1.92 (q, 3H of **9**, J = 7.0 Hz), 5.27 (dq, 2H of **8**, J = 7.0, 1.7 Hz), 5.41 (dq, 2H of **9**, J = 7.0, 1.7 Hz), 6.37 (tq, 1H of **9**, J = 7.0, 1.7 Hz), 6.46 (tq, 1H of **8**, J = 7.0, 1.7 Hz), 9.48 (s, 1H of **8**), 10.07 (s, 1H of **9**); ^{13}C NMR δ 16.81 (1C of **9**), 19.30 (1C of **8**), 67.21 (1C of **9**), 68.45 (1C of **8**), 134.82 (1C of **9**), 140.37 (1H of **8**), 140.60 (1C of **9**), 147.20 (1C of **8**), 190.33 (1C of **9**), 193.53 (1C of **8**). Anal. Calcd for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 59.85; H, 7.93.

(b) In Conditions of Thermodynamic Control. From 1.21 g (15.0 mmol) of SO_3 in 70 mL of CH_2Cl_2, 2.27 g (30.0 mmol) of EtONO in 20 mL of CH_2Cl_2, and 0.51 g (7.5 mmol) of **7** in 15 mL of CH_2Cl_2 was obtained 0.59 g (78%) of 4-hydroxy-2-methylbut-2(*E*)-enal (**8**) (eluent hexane/AcOEt = 3:1; colorless oil, R_f 0.32): IR 3600−3200, 1690, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.85 (q, 3H, J = 7.0 Hz), 5.27 (dq, 2H, J = 7.0, 1.7 Hz), 6.46 (tq, 1H, J = 7.0, 1.7 Hz), 9.48 (s, 1H); ^{13}C NMR δ 19.30, 68.45, 140.37, 147.20, 193.53. Anal. Calcd for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 59.90; H, 7.97.

(c) In Conditions of Kinetic Control at 1:1 Stoichiometry of 1 to 7. Reaction was performed according to the

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procedure given in (**a**). From 0.55 g (7.0 mmol) of SO_3 in 30 mL of CH_2Cl_2, 0.59 g (7.9 mmol) of EtONO in 15 mL of CH_2Cl_2, and 0.47 g (7.0 mmol) of **7** in 15 mL of CH_2Cl_2 was obtained crude product. This was dissolved in 50 mL of water and washed with Na_2CO_3 solution until pH 8−9, followed by extraction with $CHCl_3$ (2 × 30 mL). Solvent removal and chromatography purification gave 0.3 g (44%) of 4-methyl-1,2,6*H*-oxazine (**11**) (eluent hexane/AcOEt = 3:1; yellowish oil, R_f 0.38): IR 1667, 1555 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (s, 3H), 4.10 (d, 2H, J = 4.0 Hz), 5.52 (t, 1H, J = 4.0 Hz), 7.18 (s, 1H); ^{13}C NMR δ 18.1, 63.4, 123.5, 151.0. Anal. Calcd for C_5H_7NO: C, 61.82; H, 7.27; N, 14.43. Found: C, 61.95; H, 7.31; N, 14.52.

Reaction of 2,3-Dimethyl-1,3-butadiene (12). Reaction was performed analogously to the isoprene procedure. From 0.39 g (4.9 mmol) of SO_3 in 25 mL of CH_2Cl_2, 0.75 g (10.0 mmol) of EtONO in 25 mL of CH_2Cl_2, and 0.4 g (4.9 mmol) of **12** in 15 mL of CH_2Cl_2 was obtained 0.52 g (97%) of 4,5-dimethyl-1,2,6*H*-oxazine (**13**) (eluent hexane/AcOEt = 3:1; yellowish oil, R_f 0.40): IR 1675, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78 (s, 3H), 1.87 (s, 3H), 4.31 (s, 2H), 7.62 (s, 1H); ^{13}C NMR δ 17.1, 19.6, 66.3, 145.4. Anal. Calcd for C_6H_9NO: C, 64.82; H, 8.17; N, 12.61. Found: C, 64.72; H, 8.05; N, 12.61.

Reaction of Cyclopentadiene (15). From 1.52 g (19.0 mmol) of SO_3 in 50 mL of CH_2Cl_2, 2.12 g (28.2 mmol) of EtONO in 35 mL of CH_2Cl_2, and 0.62 g (9.4 mmol) of **15** in 20 mL of CH_2Cl_2 was obtained 0.50 g (55%) of 2-hydroxycyclopent-3-enone (**16**) (eluent hexane/AcOEt = 3:1; colorless oil, R_f 0.56): IR 3000−2870, 1755, 1647 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.84 (dd, 2H, J = 2.0, 2.0 Hz), 3.25 (m, 1H), 5.94 (ddt, 1H, J = 8.0, 2.0, 2.0 Hz), 6.14 (ddt, 1H, J = 8.0, 2.0, 2.0 Hz); ^{13}C NMR δ 43.7, 53.2, 127.1, 127.3, 202.0. Anal. Calcd for $C_5H_6O_2$: C, 61.20; H, 6.17. Found: C, 61.22; H, 6.12.

Reaction of 1,5-Cyclooctadiene (17). From 1.0 g (12.5 mmol) of SO_3 in 35 mL of CH_2Cl_2, 1.42 g (18.9 mmol) of EtONO in 30 mL of CH_2Cl_2, and 0.58 g (5.4 mmol) of **17** in 15 mL of CH_2Cl_2 was obtained 0.98 g (74%) of ethyl sulfate of 2-hydroxycyclooct-5-enone (**18**) (eluent hexane/AcOEt = 12:5; colorless oil, R_f 0.43): IR 1723, 1644 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68 (t, 3H, J = 7.0 Hz), 1.80−3.00 (m, 8H), 4.39 (q, 2H, J = 7.0 Hz), 5.18 (dd, 1H, J = 7.9, 3.9 Hz), 5.72 (dm, 1H, J = 9.0 Hz), 5,76 (dm, 1H, J = 9.0 Hz); ^{13}C NMR δ 14.1, 20.4, 22.3, 30.0, 33.5, 70.1, 81.3, 130.7, 131.8, 176.5. Anal. Calcd for $C_{10}H_{16}O_5S$: C, 48.37; H, 6.50. Found: C, 48.11; H, 6.45.

Reaction of *cis-endo*-9,10-Di(methoxycarbonyl)-tricyclo-[4.2.2.0^{2,5}]dec-3,7-diene (19). From 1.24 g (15.5 mmol) of SO_3 in 30 mL of CH_2Cl_2, 2.32 g (31.0 mmol) of EtONO in 20 mL of CH_2Cl_2, and 1.53 g (6.2 mmol) of **19**[21] in 20 mL of CH_2Cl_2 was obtained 2.2 g of crude product. Chromatography of 1.15 g of this residue (eluent hexane/AcOEt = 1:1) gave 0.95 g (76%) of ethyl sulfate of *exo*-4-hydroxy-*cis-endo*-9,10-di(methoxycarbonyl)-tricyclo[4.2.2.0^{2,5}]dec-7-en-3-one (**20**) (white crystalline powder, mp 123−129 °C with partial decomp, R_f 0.23): IR 1810, 1750, 1730, 1390, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4 (t, 3H, J = 7.0 Hz), 2.84 (dt, 1H, J = 10.0, 3.9 Hz), 2.94 (dd, 1H, J = 11.0, 1.7 Hz), 3.02 (dd, 1H, J = 11.0, 1.7 Hz), 3.34 (m, 1H), 3.45−3.56 (m, 2H), 3.57 (s, 3H), 3.59 (s, 3H), 4.35 (q, 2H, J = 7.0 Hz), 4.81 (t, 1H, J = 3.9 Hz), 6.38 (t, 1H, J = 6.9 Hz), 6.44 (t, 1H, J = 6.9 Hz); ^{13}C NMR δ 14.34, 33.38, 33.44, 34.93, 45.32, 45.61, 51.84, 61.38, 70.86, 88.54, 131.01, 132.87, 171.77, 171.92, 199.27. Anal. Calcd for $C_{16}H_{20}O_9S$: C, 49.47; H, 5.19. Found: C, 49.28; H, 5.14.

Reaction of Dicyclopentadiene (21). From 0.5 g (6.2 mmol) of SO_3 in 30 mL of CH_2Cl_2, 0.7 g (9.3 mmol) of EtONO in 30 mL of CH_2Cl_2, and 0.41 g (3.1 mmol) of **21** in 20 mL of CH_2Cl_2 was obtained 0.69 g (82%) of ethyl sulfate of *exo*-3-hydroxytricyclo[5.2.1.0^{2,6}]dec-8-en-4-one (**22**) (eluent hexane/AcOEt = 3:1; yellowish oil, R_f 0.41): IR 1773, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (dm, 1H, J = −10.4 Hz), 1.32 (dm, 1H, J = −10.4 Hz), 1.49 (t, 3H, J = 7.0 Hz), 2.87 (m, 1H), 2.91−3.00 (m, 2H), 3.25 (d, 1H, J = 4.9 Hz), 3.41−3.52 (m, 2H), 4.40 (q, 2H, J = 7.0 Hz), 4.93 (d, 1H, J = 2.8 Hz), 5.61 (dt, 1H, J = 5.8, <1 Hz), 5.76 (dt, 1H, J = 5.8, <1 Hz); ^{13}C NMR δ 15.1, 33.2, 38.0, 42.2, 48.7, 50.3, 53.3, 70.8, 81.0, 128.0, 133.3, 179.8. Anal. Calcd for $C_{12}H_{16}O_5S$: C, 52.93; H, 5.93. Found: C, 52.72; H, 5.71.

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Supporting Information Available: Optimized geometries of intermediates and transition states and the respective energies of ***I*−*XIII***. This material is available free of charge via the Internet at http://pubs.acs.org.

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