Transformation of Cycloolefins into α-Ethoxysulfo-Substituted Ketones via SO_3-Mediated Nitrosation

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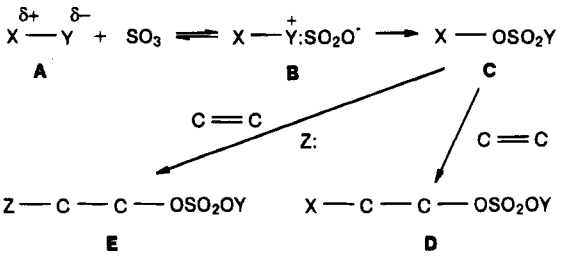
A general method for the one-pot transformation of cycloolefins into α-ethoxysulfo-substituted ketones (C=C → $EtOSO_2OCC$=O) based on SO_3-mediated nitrosation by ethyl nitrite has been developed. Examples of Wagner–Meerwein rearrangements and mechanistic rationalization for the reaction are discussed.

Electrophilic addition to an olefinic bond is a fundamental process that has seen both theoretical treatment and extensive synthetic application. Indeed, Ad_E reactions with olefins are useful means to their functionalization. Thus, the search for novel electrophilic reagents capable of adding to a C=C bond, as well as the development of methods to enhance the reactivity of unreactive electrophilic reagents, is of importance.[1-3] In recent years, we have explored a novel concept for the activation of electrophiles, namely SO_3-mediated addition (Scheme 1).[4]

The concept is based on two points. First, SO_3 can function as a Lewis acid, giving an activated complex of type **B**. Second, it is capable of inserting into an X–Y bond, which leads to a new transient reagent of type **C**.

Scheme 1

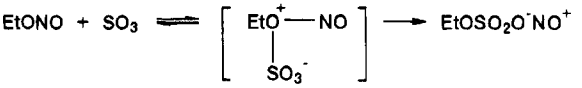


Taking into account the pronounced nucleofugal properties of YSO_2O^-,[5] the polarization in **C** should be sufficient to perform novel Ad_E reactions of type **C** → **D** and **C** → **E**. We have successfully exploited this approach for the addition of a large variety of electrophiles.[4]

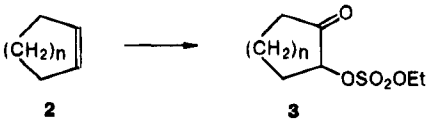
In this paper we report the application of this concept to the addition of ethyl nitrite to cycloolefins.[6,7]

Results and Discussion

We have found that ethyl nitrite reacts instantly with an equimolar amount of SO_3 at −50 to −30 °C in CH_2Cl_2 to give the highly reactive nitrosating reagent **1**.[8] Nitrosonium salts NO^+Y^- are well-known species;[9] however, to the best of our knowledge, the reagent **1** is not documented in the literature.



The reagent **1** was used *in situ*. The olefins **2a–c** in CH_2Cl_2 were added (at −50 to −30 °C, allowing the reaction mixture to rise to room temperature) to give α-ethoxysulfo ketones **3a–c**.



2 **3**

a n = 1; **b** n = 2; **c** n = 4

Two important points should be emphasized. First, although alkyl nitrites can be used as electrophilic

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(1) Schmid, G. N. Electrophilic addition to carbon-carbon double bonds. In *Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; Wiley: Chichester, U.K., 1989; Vol. 2, Part 1, p 679. Billington, D. C. *Org. React. Mech. 1984* **1986**, 385. Knipe, A. S. *Org. React. Mech. 1985* **1987**, 381. Fahey, R. C. *Top. Stereochem.* **1968**, *3*, 237.

(2) (a) Zefirov, N. S.; Zyk, N. V.; Kolbasenko, S. I.; Kutateladze, A. G. *J. Org. Chem.* **1985**, *50*, 4539 and references therein. (b) Kashman, Y.; Rudi, A. *Tetrahedron Lett.* **1979**, 1077. (c) Smit, V. A.; Zefirov, N. S.; Bodrikov, I. V.; Krimer, M. Z. *Acc. Chem. Res.* **1979**, *12*, 282. (d) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Yu. V.; Koz'min, A. S. *Zh. Org. Khim.* **1984**, *20*, 446. (e) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 2462.

(3) For selected recent examples, see: Umemoto, T.; Fukami, S.; Tomizawa, G.; Harasawa, K.; Kawada, K.; Tomita, K. *J. Am. Chem. Soc.* **1990**, *112*, 8563. Kutateladze, A. G.; Kice, J. L.; Kutateladze, T. G.; Zefirov, N. S. *J. Org. Chem.* **1993**, *58*, 995. Lal, G. S. *J. Org. Chem.* **1993**, *58*, 2791. Nenajdenko, V. G.; Gridnev, I. D.; Balenkova, E. S. *Tetrahedron* **1994**, *50*, 11023.

(4) (a) For short reviews, see: Zefirov, N. S. *Org. Synth.: Modern Trends, Proc. IUPAC Symp., 6th 1986* **1987**, 122. Chizhov, O. S., Ed.; Blackwell: Oxford, UK. (b) SO_3 + RSCl: Zefirov, N. S.; Koz'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.; Koz'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. (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*, 1126. (j) SO_3 + $R_2NSNR'_2$: Zefirov, N. S.; Zyk, N. V.; Kutateladze, A. G.; Lapin, Yu. A. *Zh. Org. Khim.* **1987**, *23*, 229. (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.

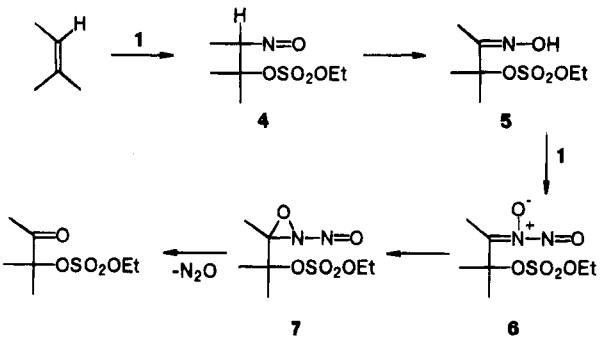
(5) Moreover, FSO_2O^- is considered as a supernucleofuge: Effenberger, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 151.

(6) Reactions of the reagent **1** with acyclic olefins and especially with terminal olefins (which give the α-sulfo-substituted aldehydes) now are under intensive investigation and will be presented in a subsequent paper.

(7) For a preliminary communication, see: Zefirov, N. S.; Zyk, N. V.; Kutateladze, A. G. *Zh. Org. Khim.* **1984**, *20*, 2473.

0022-3263/95/1960-6771$09.00/0

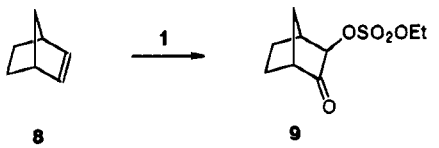
Scheme 2



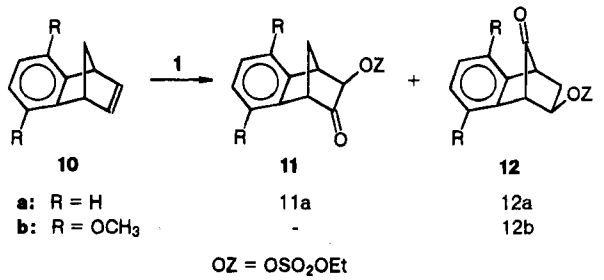
nitrosating agents, they are not capable of Ad_E reactions with olefins. Thus, this new reaction is a good demonstration of the usefulness of SO_3-mediated activation of weak electrophiles. Second, the products isolated were the ketones **3a–c**, not the corresponding nitroso compounds (**4**, Scheme 2) or oximes (**5**, Scheme 2). However, the anhydrous reaction conditions cannot support oxime hydrolysis. Careful TLC study showed that the ketones are formed at the very beginning of the process. Moreover, we first used a 1:1 stoichiometry of olefin to reagent **1**, and the yields were disappointing, never exceeding 50%.

These findings forced us to conclude that the intermediate oxime (**5**, Scheme 2) has to consume the second mole of the reagent **1** to give the final ketone, probably via the nitrosoxime **6** and oxaziridine **7**. Such a scheme has analogy in the literature.[10] It is known that oximes can be transformed into ketones by treatment with $NOBF_4$ or NO_2BF_4.[11] Indeed, we have found that at least a 1:2 ratio of olefin to reagent **1** is necessary to afford the ketones **3a–c** in comparatively high yield (*vide infra*).

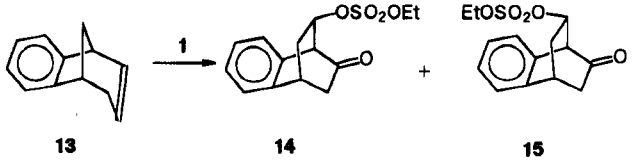
Norbornene (**8**) and its derivatives are typical strained cycloolefins that have been widely used for rearrangement studies of electrophilic additions. It is documented, however, that the reactions of NOCl[12] and related reagents (ONOCOH,[13] *etc.*) with these olefins proceed as *exo-cis* additions without skeletal rearrangement. Moreover, the cases of Wagner–Meerwein rearrangements are extremely rare and have been observed only for very specific structures that are especially prone to rearrangements.[14] The reaction of norbornene with the reagent **1** gives nonrearranged ketone **9** with the *exo* configuration of the substituent.



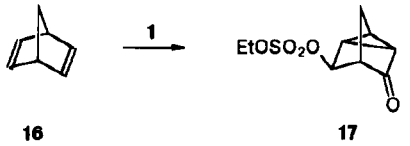
However, the analogous reaction of benzonorbornadiene (**10a**) gave a 2:3 mixture of rearranged (**12a**) and nonrearranged (**11a**) ketones. In the case of dimethoxyolefin **10b**, only the product of Wagner–Meerwein rearrangement, **12b**, was isolated.



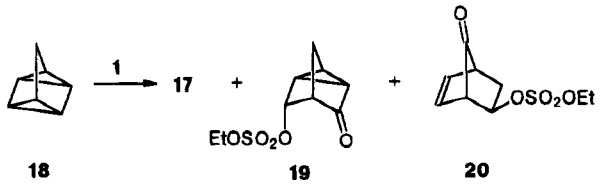
Benzobicyclo[3.2.1]octa-2,6-diene (**13**) reacts with **1** exclusively by Wagner–Meerwein rearrangement to give a mixture of two stereoisomeric ketones **14** and **15**.[15]



We now consider the addition to norbornadiene (**16**). Transannular ring closure to give nortricyclane derivatives is a common feature of the addition of "effectively strong electrophiles" (for definition see ref 16) to this diene.[17] We have found that the addition of **1** to **16** gives only **17**, with participation of the second double bond.



Treatment of quadricyclane (**18**) with **1** results in smooth cleavage of the cyclopropane ring but gives different results: the products are the stereoisomeric ketones **17** and **19** and rearranged unsaturated ketone **20**.



The results of this study clearly show that the EtONO + SO_3 addition to cycloolefins is an effective new electrophilic Ad_E reaction. The one-pot EtONO + SO_3 addition offers a practical, versatile, and inexpensive way

(8) A low-temperature ^{15}N NMR (CD_2Cl_2, CH_3NO_2 as internal standard) spectrum of the 1 shows a signal at δ −5.6 ppm (*cf.* $NOBF_4$ in liquid SO_2, δ −0.4 ppm: Olah, G. A.; Gupta, B. B. G.; Narang, S. C. *J. Am. Chem. Soc.* **1979**, *101*, 5317).

(9) Some of the most common nitrosonium salts are the following: $Y^- = BF_4^-$, PF_6^-, ClO_4^-, SbF_6^-, $AlCl_4^-$, HSO_4^-.

(10) Wieland, T.; Grimm, D. *Chem. Ber.* **1963**, *96*, 275. Kliegman, J. M.; Barnes, R. K. *J. Org. Chem.* **1972**, *37*, 4223. Kyung, J. H.; Clapp, L. B. *J. Org. Chem.* **1976**, *41*, 2024.

(11) Olah, G. A.; Ho, T.-L. *Synthesis* **1976**, *9*, 610.

(12) (a) Ponder, P. W.; Wheat, P. W. *J. Org. Chem.* **1975**, *37*, 543. Miller, J. B. *J. Org. Chem.* **1961**, *26*, 4905. (b) Meinwald, J.; Meinwald, Y. C.; Baker, T. N. *J. Am. Chem. Soc.* **1963**, *85*, 2513. (c) Della, E. W.; Reimerink, M. P.; Wright, B. G. *Aust. J. Chem.* **1979**, *32*, 2235.

(13) Hamann, H. C.; Swern, D. *J. Am. Chem. Soc.* **1968**, *90*, 6481.

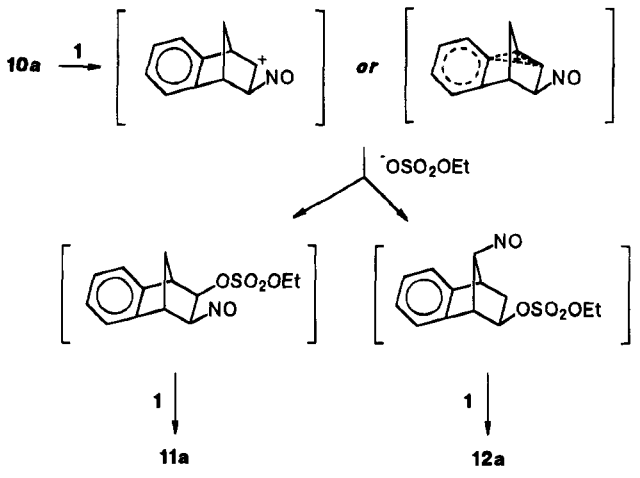
(14) Markowicz, S. W. *Rocz. Chem.* **1975**, *49*, 2117. Broxterman, Q. B.; Hogeveen, H.; Klingma, R. F.; van Bolhius, F. *J. Am. Chem. Soc.* **1985**, *107*, 5722. Yadav, J. S.; Chawla, H. P. C.; Dev Sukh; Rao, A. S. C. P.; Nayak, U. R. *Tetrahedron* **1977**, *33*, 2441.

(15) The configurational assignment of the stereoisomers **14** and **15** was performed on the basis of the low-field shift of the HCO proton of compound **14** in the ^1H NMR spectrum connected with the magnetic anisotropy of the carbonyl group: Günther, H. *NMR Spectroscopy. An Introduction*; Wiley: Chichester, New York, 1980.

(16) (a) See ref 2a. (b) Zefirov, N. S.; Bodrikov, I. V. *Zh. Org. Khim.* **1983**, *19*, 2225. (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.

(17) Zefirov, N. S.; Sadovaja, N. K.; Achmedova, R. Sh.; Bodrikov, I. V.; Morrill, T. C.; Nersisyan, A. M.; Rybakov, W. B.; Saraceno, N. D.; Struchkov, Yu. T. *Zh. Org. Khim.* **1980**, *16*, 580. Zefirov, N. S.; Zyk, N. V.; Nikulin, A. V. *Zh. Org. Khim.* **1981**, *17*, 1105.

Scheme 3



of functionalizing cycloolefins into α-ethoxysulfo-substituted ketones, C=C → $EtOSO_2OCC=O$. This reaction is of potential synthetic utility, especially since the OSO_2OEt group is highly nucleofugic and is capable of nucleophilic substitution.[18]

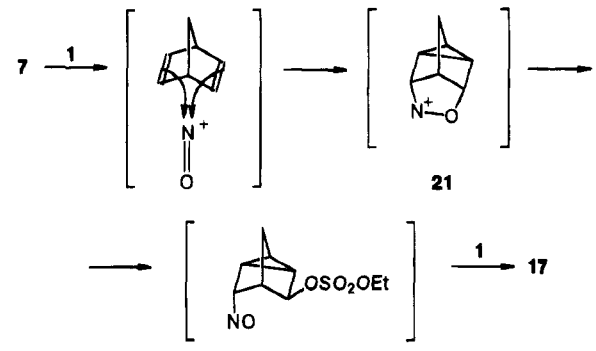
In spite of somewhat conflicting opinions about the mechanism of nitrosation of olefins,[19] there can be little doubt that the reaction involves an electrophilic attack of nitrosonium cation as a first step, followed by either attack by a counterion to give the 1,2-addition product or C–C bond participation to give rearranged product(s). One may speculate on the intermediacy of nonclassical cations especially for the cases of homobenzilic or homoallylic participation. The ratio of rearranged products increased with the increasing stability of the intermediate cation. This statement is clearly demonstrated by the olefins in the bicyclo[2.2.1]heptane series: in going from norbornene (**8**) to benzonorbornadiene (**10a**) and then to 3,6-dimethoxybenzonorbornadiene (**10b**), the portion of rearranged products drastically increases (from 0 to 100%). The mechanistic rationalization for the case of olefin **10a** is shown in Scheme 3.

In the case of quadricyclane, the primary attack of nitrosonium cation occurs at the apex of the cyclopropane ring,[20] ultimately with the formation of the usual products **17**, **19**, and **20**. This observation indicates rather high "effective electrophilicity" of the reagent **1**.

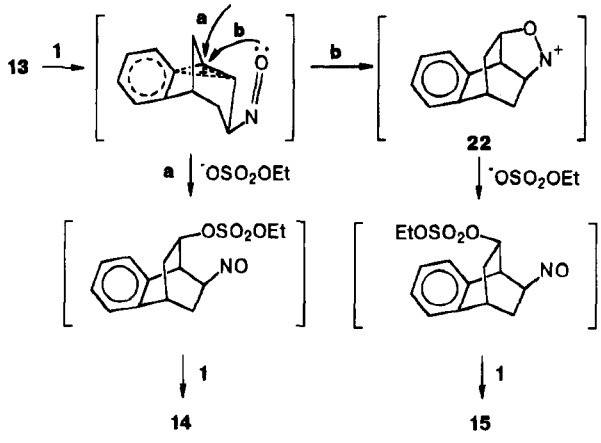
It should be noted that the configurational assignment of 3,5-disubstituted nortricyclanes is not a simple matter (*cf.* ref 21). For this purpose, we have used the method based on the magnitude of heteronuclear spin–spin coupling constants ^3J ($^1H_5$–$^{13}C_3$)[22] for the compounds **17** and **19**.

Since the reaction of reagent **1** with quadricyclane showed a lack of stereospecificity in the final attack by sulfate anion, the stereospecific formation of a single product in the case of the reaction of **1** with norborna-

Scheme 4



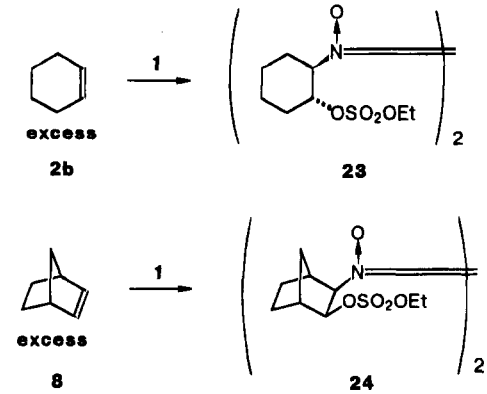
Scheme 5



diene (**16**) is rather unexpected.[23] This stereospecificity is probably an indication of a primary attack by the electrophile from the *endo* side, as presented in Scheme 4.

Analogously, the absence of stereospecificity in the reaction of **1** with olefin **13** can be explained in terms of the formation of cyclic intermediate **22** (Scheme 5, *cf.* with intermediate **21**). This scheme is confirmed by results of bromination, chlorination, and chlorosulfamination[24] of olefin **13**, where only a single isomer is observed because the formation of a cyclic intermediate of type **22** is impossible.

As mentioned above, the suggested reaction mechanism includes the nitrosation of the intermediate oxime **5** (Scheme 2) by the second equivalent of the reagent **1**. Therefore, the first stage of the reaction must be the formation of nitroso compounds **4**. We have confirmed this experimentally by using a large excess of olefin to stop the reaction at the primary adduct stage. Indeed, we were able to isolate the unstable dimeric nitrososulfates **23** and **24**.



(18) Robertson, R. E.; Sugamory, S. E. *Can. J. Chem.* **1966**, *44*, 1728. Kolesnikov, V. A.; Efremov, R. V.; Danov, S. M.; Gryazneva, L. V. *Kinet. Katal.* (*Russ.*) **1977**, *18*, 1065.

(19) (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) See ref 12b.

(20) Bealieu, P. L.; Morisset, V. M.; Garratt, D. E. *Can. J. Chem.* **1980**, *58*, 1005. Bealieu, P. L.; Kabo, A.; Garratt, D. E. *Can. J. Chem.* **1980**, *58*, 1014. Sadovaja, N. K.; Velikokhat'ko, T. N.; Zefirov, N. S. *Zh. Org. Khim.* **1983**, *19*, 241.

(21) Chizhov, A. O.; Zefirov, N. S.; Zyk, N. V. *J. Org. Chem.* **1987**, *52*, 5647.

(22) Chizhov, A. O.; Zyk, N. V.; Okhanov, V. V.; Zefirov, N. S. *Dokl. Akad. Nauk SSSR* **1983**, *271*, 1405.

In conclusion, we have developed a method for the one-pot transformation of cycloolefins into α-sulfosubstituted ketones that clearly demonstrates the usefulness of the SO_3 activation of weak electrophiles in organic synthesis.[25]

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$. All reactions were followed by TLC with precoated aluminum TLC plates (silica gel, Silufol, Czechoslovakia). Preparative column chromatography involved silica gel (40/100 μm or Silpearl) and ethyl acetate–hexane mixtures as the eluent. All solvents and reagents were additionally purified and dried by standard techniques. Ethyl nitrite was synthesized as previously reported.[26] SO_3 was obtained from 60% oleum. Freshly distilled SO_3 was used, which was weighed and dissolved in CH_2Cl_2.

General Procedure for the Addition Reaction (Excess of Reagent 1). A dry three-necked flask fitted with an addition funnel, stirrer, and argon inlet was charged with 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, keeping the temperature at −50 to −30 °C. The resulting mixture was stirred 0.5 h at this temperature, and a solution of olefin in CH_2Cl_2 was added dropwise at −50 to −30 °C. The workup involved stirring for 1 h at −50 °C and 0.5 h at rt, treatment with cold water, extraction with $CHCl_3$, and drying over $MgSO_4$. After rotatory evaporation of the solvent the crude adduct was chromatographed.

Reaction of Cyclopentene (2a). From 1.14 g (14.3 mmol) of SO_3 in 20 mL of CH_2Cl_2, 2.13 g (28.4 mmol) of EtONO in 20 mL of CH_2Cl_2, and 0.39 g (5.7 mmol) of **2a** in 15 mL of CH_2Cl_2 was obtained 0.74 g (62%) of the ethyl sulfate of 2-hydroxycyclopentanone (**3a**) (eluent hexane:AcOEt = 2:1; yellowish oil, R_f 0.30): IR 1774, 1400, 1200 cm^{-1}; mass spectrum (*m/z*) 208 (M^+); ^1H NMR ($CDCl_3$) δ 1.38 (t, 3H, *J* = 7.1 Hz), 1.68–2.83 (m, 6H), 4.46 (m, 2H), 4.80 (dd, 1H, *J* = 6.6, 6.0 Hz); ^{13}C NMR δ 14.5, 16.8, 29.2, 34.5, 70.7, 82.2, 209.0. Anal. Calcd for $C_7H_{12}O_5S$: C, 40.38; H, 5.81. Found: C, 40.05; H, 5.71.

Reaction of Cyclohexene (2b). From 2.25 g (28.3 mmol) of SO_3 in 100 mL of CH_2Cl_2, 4.25 g (56.5 mmol) of EtONO in 60 mL of CH_2Cl_2, and 0.93 g (11.3 mmol) of **2b** in 30 mL of CH_2Cl_2 was obtained 2.37 g (94%) of the ethyl sulfate of 2-hydroxycyclohexanone (**3b**) (eluent hexane:AcOEt = 3:1; yellowish oil, R_f 0.13): IR 1733, 1400, 1196 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (t, 3H, *J* = 7.1 Hz), 1.89–2.47 (m, 8H), 4.40 (q, 2H, *J* = 7.1 Hz), 4.96 (m, 1H); ^{13}C NMR δ 14.3, 23.2, 26.6, 34.2, 40.7, 70.5, 83.8, 202.3. Anal. Calcd for $C_8H_{14}O_5S$: C, 43.23; H, 6.35. Found: C, 43.52; H, 6.27.

Reaction of Cyclooctene (2c). From 0.61 g (7.6 mmol) of SO_3 in 20 mL of CH_2Cl_2, 1.15 g (15.3 mmol) of EtONO in 15 mL of CH_2Cl_2, and 0.34 g (3.0 mmol) of **2c** in 15 mL of CH_2Cl_2 was obtained 0.44 g (58%) of the ethyl sulfate of 2-hydroxycyclooctanone (**3c**) (eluent heptane:AcOEt = 1:1; yellowish oil, R_f 0.62): IR 1715, 1400 1200 cm^{-1}; mass spectrum (*m/z*) 250 (M^+); ^1H NMR ($CDCL_3$) δ 1.39 (t, 3H, *J* = 7.1 Hz), 1.75–2.60 (m, 12H), 4.40 (m, 2H), 4.92 (m, 1H).

Reaction of Norbornene (8). From 1.48 g (18.5 mmol) of SO_3 in 30 mL of CH_2Cl_2, 1.74 g (23.1 mmol) of EtONO in 20 mL of CH_2Cl_2, and 0.87 g (9.3 mmol) of **8** in 20 mL of CH_2Cl_2 was obtained 1.80 g of crude product. Chromatography of 0.98 g of this residue gave 0.66 g (56%) of the ethyl sulfate of *exo*-3-hydroxybicyclo[2.2.1]heptan-2-one (**9**) (eluent hexane:AcOEt = 3:1; yellowish oil, R_f 0.43): IR 1770, 1400, 1200 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.41 (t, 3H, *J* = 7.1 Hz), 1.44–1.56 (m, 2H), 1.63 (dm, 1H, *J* = −11 Hz), 1.76–1.93 (m, 2H), 2.12 (dm, 1H, *J* = −11 Hz), 2.63 (m, 1H), 2.86 (m, 1H), 4.19 (s, 1H), 4.38 (m, 2H); ^{13}C NMR δ 14.2, 23.1, 23.3, 33.7, 40.3, 47.6, 70.4, 82.2, 208.4. Anal. Calcd for $C_9H_{14}O_5S$: C, 46.14; H, 6.02. Found: C, 46.34; H, 5.91.

Reaction of Benzonorbornadiene (10a). From 0.30 g (3.8 mmol) of SO_3 in 20 mL of CH_2Cl_2, 0.35 g (4.7 mmol) of EtONO in 20 mL of CH_2Cl_2, and 0.27 g (11.3 mmol) of **10a**[27] in 20 mL of CH_2Cl_2 was obtained 0.5 g of crude product, which upon chromatography (eluent hexane:AcOEt = 3:1) gave (a) 0.2 g (38%) of the ethyl sulfate of *exo*-10-hydroxytricyclo-[6.2.1.$0^{2,7}$]undeca-2(7),3,5-trien-9-one (**11a**) [yellowish oil, R_f 0.57, IR 1770, 1400, 1200 cm^{-1}; mass spectrum (*m/z*) 282 (M^+); ^1H NMR ($CDCl_3$) δ 1.29 (t, 3H, *J* = 7.1 Hz), 2.5 (m, 2H), 3.44 (s, 1H), 3.79 (s, 1H), 4.28 (s, 1H), 4.38 (q, 2H, *J* = 7.1 Hz), 7.25 (m, 4H). Anal. Calcd for $C_{13}H_{14}O_5S$: C, 55.31; H, 5.00. Found: C, 55.14; H, 4.95] and (b) 0.12 g (23%) of the ethyl sulfate of *exo*-9-hydroxytricyclo[6.2.1.$0^{2,7}$]undeca-2(7),3,5-trien-11-one (**12a**) [yellowish oil, R_f 0.31; IR 1800, 1400, 1200 cm^{-1}; mass spectrum (*m/z*) 282 (M^+); ^1H NMR ($CDCl_3$) δ 1.38 (t, 3H, *J* = 7.1 Hz), 1.67–2.33 (m, 2H), 3.38 (d, 1H, *J* = 3.8 Hz), 3.75 (s, 1H), 4.38 (q, 2H, *J* = 7.1 Hz), 4.71 (dd, 1H, *J* = 7.8, 3.8 Hz), 7.25 (m, 4H). Anal. Calcd for $C_{13}H_{14}O_5S$: C, 55.31; H, 5.00. Found: C, 55.21; H, 4.97].

Reaction of 3,6-Dimethoxybenzonorbornadiene (10b). From 0.36 g (4.5 mmol) of SO_3 in 25 mL of CH_2Cl_2, 0.84 g (11.2 mmol) of EtONO in 30 mL of CH_2Cl_2, and 0.46 g (2.3 mmol) of **10b**[28] in 20 mL of CH_2Cl_2 was obtained 0.74 g of crude product. Chromatography of 0.63 g of this residue (eluent hexane:AcOEt = 2:1) gave 0.42 g (64%) of the ethyl sulfate of 3,6-dimethoxy-*exo*-9-hydroxytricyclo[6.2.1.$0^{2,7}$]undeca-2(7),3,5-trien-11-one (**12b**) (yellowish oil, R_f 0.25): IR 1800, 1405, 1200 cm^{-1}; mass spectrum (*m/z*) 342 (M^+); ^1H NMR ($CDCl_3$) δ 1.46 (t, 3H, *J* = 7.1 Hz), 2.23 (dd, 1H, *J* = −14.0, 7.4 Hz), 2.30 (ddd, 1H, *J* = −14.0, 5.5, 3.2 Hz), 3.77 (s, 6H), 3.85 (m, 1H), 3.95 (s, 1H), 4.36 (q, 1H, *J* = 7.1 Hz), 4.73 (dd, 1H, *J* = 7.4, 3.2 Hz), 6.68 (s, 2H); ^{13}C NMR δ 14.6, 33.3, 43.2, 49.9, 56.0 (2C), 70.3, 79.4, 110.2, 111.1, 122.7, 130.4, 147.8, 149.2, 199.5. Anal. Calcd for $C_{15}H_{18}O_7S$: C, 52.62; H, 5.30. Found: C, 52.57; H, 5.30.

Reaction of Benzobicyclo[3.2.1]octa-2,6-diene (13). From 0.81 g (10.0 mmol) of SO_3 in 30 mL of CH_2Cl_2, 1.51 g (20.0 mmol) of EtONO in 15 mL of CH_2Cl_2, and 0.63 g (4.0 mmol) of **13**[24a] in 20 mL of CH_2Cl_2 was obtained 0.59 g of crude product. Chromatography of 0.22 g of this residue (eluent hexane:AcOEt:$CHCl_3$ = 10:7:30) gave (a) 0.12 g (27%) of the ethyl sulfate of *exo*-11-hydroxytricyclo[6.2.2.$0^{2,6}$]dodeca-2(7),3,5-trien-9-one (**14**) [yellowish oil, R_f 0.68; IR 1740, 1400, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (t, 3H, *J* = 7.1 Hz), 2.0–2.5 (m, 4H), 3.43 (m, 1H), 4.01 (d, 1H, *J* = 4.1 Hz), 4.33 (m, 2H), 5.02 (ddd, 1H, *J* = 9.3, 4.1, 2.2 Hz), 7.2 (m, 4H); ^{13}C NMR δ 14.6, 34.4, 36.6, 40.8, 57.5, 70.4, 80.7, 124.0, 127.3, 127.7, 128.8, 130.7, 142.6, 206.0. Anal. Calcd for $C_{14}H_{16}O_5S$: C, 56.74; H, 5.44. Found: C, 56.57; H, 5.44] and (b) 0.1 g (21%) of the *endo* isomer **15** [yellowish oil, R_f 0.25; IR 1740, 1400, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (t, 3H, *J* = 7.1 Hz), 1.84–2.63 (m, 4H), 3.28 (m, 1H), 4.05 (d, 1H, *J* = 3.5 Hz), 4.32 (m, 2H), 4.83 (ddd, 1H, *J* = 9.8, 3.5, 3.5 Hz), 7.18 (m, 4H); ^{13}C NMR δ 14.6, 31.4, 34.1, 34.2, 46.6, 70.1, 80.5, 123.9, 126.1, 127.4, 128.2, 133.7, 142.7, 156.7. Anal. Calcd for $C_{14}H_{16}O_5S$: C, 56.74; H, 5.44. Found: C, 56.65; H, 5.90].

Reaction of Norbornadiene (16). From 1.49 g (18.6 mmol) of SO_3 in 30 mL of CH_2Cl_2, 2.80 g (37.3 mmol) of EtONO in 20 mL of CH_2Cl_2, and 0.69 g (7.5 mmol) of **16** in 15 mL of CH_2Cl_2 was obtained 1.62 g of crude product, which upon chromatography (eluent hexane:AcOEt = 2:1) gave 0.65 g (37%) of the ethyl sulfate of *exo*-5-hydroxytricyclo[2.2.1.$0^{2,6}$]-

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(25) Some examples of the synthetic application of this reaction (*e.g.* in the synthesis of α,β-unsaturated ketones, synthesis of heterocyclic compounds, *etc.*) will be given in a subsequent paper.

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heptan-3-one (**17**) (yellowish oil, R_f 0.30): IR 1770, 1410, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (t, 3H, J = 7.1 Hz), 1.76 (dd, 1H, J = 6.0, 6.0 Hz), 2.07 (dt, 1H, J = −11.2, 1.5 Hz), 2.25 (dt, 1H, J = −11.2, 1.5 Hz), 2.35 (broad s, 1H), 2.44 (ddm, 1H, J = 6.0, 6.0 Hz), 2.59 (dddd, 1H, J = 6.0, 6.0, 1.6, 1.6 Hz), 4.32 (m, 2H), 4.95 (t, 1H, J = 2.0 Hz); ^{13}C NMR δ 14.6, 20.7, 25.2, 25.5, 28.8, 43.2, 69.9, 81.7, 204.2. Anal. Calcd for $C_9H_{12}O_5S$: C, 46.54; H, 5.21. Found: C, 46.09; H, 5.37.

Reaction of Quadricyclane (18). From 1.26 g (15.8 mmol) of SO_3 in 30 mL of CH_2Cl_2, 2.37 g (31.6 mmol) of EtONO in 20 mL of CH_2Cl_2, and 0.58 g (6.3 mmol) of **18**[29] in 20 mL of CH_2Cl_2 was obtained 1.38 g of crude product, which upon chromatography (eluent hexane:AcOEt = 3:2) gave (a) 0.07 g (5%) of the ethyl sulfate of *exo*-5-hydroxybicyclo[2.2.1]hept-2-en-7-one (**20**) [yellowish oil, R_f 0.47; IR 1790, 1640, 1410, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.41 (t, 3H, J = 7.1 Hz), 1.96–2.14 (m, 2H), 3.00 (ddm, 1H, J = 3.4, 3.4 Hz), 3.35 (d, 1H, J = 3.6 Hz), 4.35 (q, 2H, J = 7.1 Hz), 4.72 (ddd, 1H, J = 8.6, 2.6, 1.0 Hz), 6.41 (dddd, 1H, J = 7.2, 3.4, 1.2, 0.5 Hz), 6.76 (ddd, 1H, J = 7.2, 3.6, 0.8 Hz); ^{13}C NMR δ 14.5, 31.6, 44.3, 51.3, 70.0, 79.3, 128.4, 138.1, 200.0. Anal. Calcd for $C_9H_{12}O_5S$: C, 46.54; H, 5.21. Found: C, 46.28; H, 5.30] and (b) 0.47 g (32%) of a mixture of compounds **17** and **19** (1:1) [yellowish oil, R_f 0.37; IR 1770, 1410, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38–1.48 (m, 6H of **17** and **19**), 1.64 (dd, 1H of **19**, J = 6.0, 6.0 Hz), 1.76 (dd, 1H of **17**, J = 6.0, 6.0 Hz), 1.96 (dt, 1H of **19**, J = −11.2, 1.6 Hz), 2.07 (dt, 1H of **17**, J = −11.2, 1.5 Hz), 2.11 (dt, 1H of **19**, J = −11.2, 1.6 Hz), 2.23 (broad s, 1H of **19**), 2.25–2.31 (m, 2H of **17** and **19**), 2.35 (broad s, 1H of **17**), 2.44 (ddm, 1H of **17**, J = 6.0, 6.0 Hz), 2.53 (dddd, 1H of **19**, J = 6.0, 6.0, 2.0, 1.0 Hz), 2.59 (dddd, 1H of **17**, J = 6.0, 6.0, 1.6, 1.6 Hz), 4.27–4.41 (m, 4H of **17** and **19**), 4.95 (t, 1H of **17**, J = 2.0 Hz), 5.08 (t, 1H of **19**, J = 2.0 Hz); ^{13}C NMR δ 14.5 (1C of **19**), 14.6 (1C of **17**), 17.6 (1C of **19**), 17.7 (1C of **19**), 20.7 (1C of **17**), 23.1 (1C of **19**), 25.2 (1C of **17**), 25.5 (1C of **17**), 28.0 (1C of **19**), 28.8 (1C of **17**), 41.7 (1C of **19**), 43.2 (1C of **17**), 69.9 (1C of **17**), 70.3 (1C of **19**), 81.7 (1C of **17**), 86.8 (1C of **19**), 204.2 (1C of **17**), 208.8 (1C of **19**). Anal. Calcd for $C_9H_{12}O_5S$: C, 46.54; H, 5.21. Found: C, 46.40; H, 5.12.

General Procedure for Addition Reaction (Excess of the Olefin). A dry three-necked flask fitted with an addition funnel, stirrer, argon inlet, and thermometer 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, keeping this temperature. The resulting mixture was stirred 0.5 h at −50 °C; then the temperature was decreased to −85 °C and a solution of olefin in a minimal amount of CH_2Cl_2 was added rapidly. The workup involved stirring 0.5 h at −50 °C and 0.5 h at the room temperature. After rotary evaporation of the solvent and excess of olefin, the crude product was purified by recrystallization from ethanol.

Reaction of Cyclohexene (2b). From 1.56 g (19.5 mmol) of SO_3 in 80 mL of CH_2Cl_2, 3.0 g (40.0 mmol) of EtONO in 35 mL of CH_2Cl_2, and 16.0 g (195.0 mmol) of **2b** (without solvent) was obtained 3.88 g of a dark oil. Then 0.29 g of crude product was dissolved in 5 mL of EtOH; after that white crystals precipitated from the solution, which were filtered, washed with EtOH, and dried in vacuum. After this workup 0.04 g (13%) of the *trans* dimer of the ethyl sulfate of *trans*-2-hydroxynitrosocyclohexane (**23**) was obtained: IR 1460, 1400, 1200, 1240 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.4 (t, 3H, J = 7.1 Hz), 1.85–2.52 (m, 8H), 4.31 (m, 2H), 5.07 (ddd, 1H, J = 12.5, 12.5, 4.5 Hz), 5.48 (ddd, 1H, J = 12.5, 12.5, 4.5 Hz). Anal. Calcd for $C_{16}H_{30}N_2O_{10}S_2$: C, 40.50; H, 6.37; N, 5.90. Found: C, 41.45; H, 6.43; N, 6.05.

Reaction of Norbornene (8). From 0.32 g (4.0 mmol) of SO_3 in 30 mL of CH_2Cl_2, 0.60 g (8.0 mmol) of EtONO in 15 mL of CH_2Cl_2, and 3.76 g (40.0 mmol) of **8** in 3 mL of CH_2Cl_2 was obtained 0.66 g (71%) of the *trans* dimer of the ethyl sulfate of *cis-exo*-3-hydroxy-2-nitrosobicyclo[2.2.1]heptane (**24**) (white crystals, R_f 0.15 (eluent hexane:AcOEt = 3:1)): IR 1460, 1380, 1200, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (t, 3H, J = 7.1 Hz), 1.5–1.8 (m, 4H), 2.00–2.04 (m, 2H), 2.66 (dd, 1H, J = 4.2, 1.5 Hz), 2.74 (dd, 1H, J = 4.2, 1.5 Hz), 4.30 (m, 2H), 4.85 (dd, 1H, J = 6.6, 1.8 Hz), 4.95 (dd, 1H, J = 6.6, 1.8 Hz); ^{13}C NMR δ 14.6, 23.2, 25.8, 36.0, 38.2, 40.7, 69.9, 72.5, 84.3. Anal. Calcd for $C_{18}H_{30}N_2O_{10}S_2$: C, 43.37; H, 6.07; N, 5.62. Found: C, 43.11; H, 5.97; N, 5.67.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **14** and **15** (5 pages). This material is contained in libraries on microfiche, immediatelly follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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