Sulfur Trioxide Assisted Electrophilic Addition of R_2NCl to Olefins

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The one-pot reaction of SO_3, *N,N*-dialkylchloroamines, and olefins gives *N,N*-dialkylsulfamates of the corresponding chlorohydrins (**6**). These additions are shown to have electrophilic character. Experimental evidence supports the principle that SO_3 increases the effective electrophilicity of weak electrophiles.

Electrophilic addition to a double bond (eq 1 and 2) is the one of the basic processes in organic chemistry that has fundamental theoretical value and extensive synthetic applications.[1] The addition of an electrophile $X^{\delta+}$–$Y^{\delta-}$ to

$$X^{\delta+}-Y^{\delta-} + C{=}C \longrightarrow X-C-C-Y \qquad (1)$$

$$X^{\delta+}-Y^{\delta-} + C{=}C \bullet Z^- \longrightarrow X-C-C-Z \qquad (2)$$

a C=C bond to give a 1,2-disubstituted ethane is a useful way to functionalize an olefin. The search for new electrophilic reagents capable of adding to a C=C bond[2] and for novel types of conjugated additions incorporating an external nucleophile[3,4] in accordance with eq 2 are matters of importance.

Decisive factors for electrophilic reactivity of an electrophile $X^{\delta+}$–$Y^{\delta-}$ are (i) the degree of polarization (up to dissociation) of X–Y bond (Chart I) and (ii) the "intrinsic" electrophilicity of bare cationic species X^+, which determine the upper limit of electrophilic reactivity of all X^+-containing reagents. Several approaches have been suggested to enhance the reactivity of electrophilic reagents.

First is the use of the solvents with increased polarity or enhanced "ionizing power",[5] which provides the necessary energy for dissociation and promotes a more ionic pathway. There are many examples of solvent influence on electrophilic additions. For instance, hypohalites fail to react with most alkenes by an ionic mechanism in aprotic nonpolar solvents but do react in polar solvents.[6] Similarly, the use of formic acid as a solvent increases the "effective electrophilicity"[7] of RSCl in addition reactions to olefins.[8]

Chart I

$$X^{\delta+}{-}Y^{\delta-} \rightleftharpoons X^+\,Y^- \rightleftharpoons X^+ + Y^-$$

increasing of electrophilicity and effective electrophilicity

Scheme I

$$X^{\delta+}{-}Y^{\delta-} \bullet SO_3 \longrightarrow \underset{1}{\left[X^{\delta+}{-}\overset{\delta-}{O}SO_2Y\right]} \xrightarrow{C=C} \underset{2}{X-C-C-OSO_2Y} \quad \underset{3}{X-C-C-Z} \;(Z^-)$$

Second, a frequently employed means for increasing the reactivity of electrophiles is catalysis by Lewis acids (eq 3). This approach has been considered in detail,[1,2a,6,9] and we shall only point out the example of the BF_3 catalysis of the ionic reaction of methyl hypochlorite with olefins to give fluoro and methoxy chlorides.[6]

$$X^{\delta+}{-}Y^{\delta-} + MY_n \longrightarrow X^+[MY_{n+1}]^- \qquad (3)$$

MY_n = BF_3, SbF_5, $AlCl_3$ etc.

Third, the course of electrophilic additions can be changed by the addition of electrolytes.[10–13] We have previously shown that the addition of a large amount of $LiClO_4$ to the reaction of ArSCl with olefins provides a "doping effect": a dramatic increase in the effective electrophilicity of the reagent.[7,10–13] Exploration of the doping addition principle in ArSCl reactions permitted us to obtain products of skeletal rearrangements,[10–12] of series of skeletal rearrangements,[12] of hydride shifts,[13] and of new types of 1,2-additions.[4c,10] Certain additions occur only in

(1) De la Mare, P. B. D. "Electrophilic Halogenation"; Cambridge University Press: Cambridge, 1976. De la Mare, P. B. D.; Bolton, R. "Electrophilic Additions to Unsaturated Systems"; Elsevier: Amsterdam, 1966. Fahey, R. S. *Top. Stereochem.* **1968**, *3*, 273. Traylor, T. S. *Acc. Chem. Res.* **1969**, *2*, 152. Patai, S., Ed. "The Chemistry of Double Bonded Functional Groups"; Wiley: New York, 1977.

(2) (a) For superb review, see: Effenberger, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 151. (b) For selected recent examples, see: Buddrus, J.; Plettenberg, H. *Chem. Ber.* **1980**, *113*, 1494. Trost, B. M.; Shibata, T.; Martin, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 3228. Caserio, M.; Kim, J. K. *Ibid.* **1982**, *104*, 3231. Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Tetrahedron Lett.* **1982**, *23*, 1361. Miyaura, N.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 2368. Bäckvall, J.-E.; Bergman, J.; Engman, L. *J. Org. Chem.* **1983**, *48*, 3918. Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Yu. V.; Koz'min, A. S. *Zh. Org. Khim.* **1984**, *20*, 446. Engman, L. *J. Am. Chem. Soc.* **1984**, *106*, 3977. Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 2462. Schastin, A. B.; Balenkova, E. S. *Zh. Org. Khim.* **1984**, *20*, 956.

(3) For selected examples, see: Olah, G.; Gupta, B. *Synthesis* **1980**, 44. Cambie, R. C.; Larsen, D. S.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 1* **1981**, 58. Hayama, T.; Tomoda, Sh.; Takeuchi, Y.; Nomura, Y. *Tetrahedron Lett.* **1982**, *23*, 4733. Bloodworth, A. J.; Courtneidge, J. L. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1797, 1807. Larock, R. C. *Tetrahedron* **1982**, *38*, 1713. Zefirov, N. S.; Velikokhat'ko, T. N.; Sadovaja, N. K. *Zh. Org. Khim.* **1983**, *19*, 1593. Toshimitsu, A.; Uemura, S.; Okano, M. *J. Org. Chem.* **1983**, *48*, 5246. Barluenga, J.; Jimenez, C.; Majera, C.; Yus, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 591. Ting, P. S.; Bartlett, P. A. *J. Am. Chem. Soc.* **1984**, *106*, 2668.

(4) (a) For an overview, see: Zefirov, N. S.; Koz'min, A. S.; Zhdankin, V. V.; Kirin, V. N.; Yur'eva, N. M.; Sorokin, V. D. *Chem. Scr.* **1983**, *22*, 195. (b) Zefirov, N. S.; Koz'min, A. S.; Zhdankin, V. V.; Nikulin, A. V.; Zyk, N. V. *J. Org. Chem.* **1982**, *47*, 3679. Zefirov, N. S.; Zhdankin, V. V. *Tetrahedron* **1982**, *38*, 291. (c) Zefirov, N. S.; Sadovaja, N. K.; Maggerramov, A. M.; Bodrikov, I. V. *Zh. Org. Khim.* **1977**, *13*, 245.

(5) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

(6) Heasley, V. L.; Gipe, R. K.; Martin, J. L.; Wiese, H. C.; Oakes, M. L.; Shellhamer, D. F. *J. Org. Chem.* **1983**, *48*, 3195.

(7) (a) Zefirov, N. S.; Bodrikov, I. V. *Zh. Org. Khim.* **1983**, *19*, 2225. (b) See also ref 15 in: Zefirov, N. S.; Zyk, N. V.; Borisenko, A. A.; Krysin, M. Yu.; Schestakova, T. G. *Tetrahedron* **1983**, *39*, 3145.

(8) Zefirov, N. S.; Sadovaja, N. K.; Novgorodtseva, L. A.; Bodrikov, I. V. *Tetrahedron* **1978**, *34*, 1373. Zefirov, N. S.; Sadovaja, N. K.; Novgorodtseva, L. A.; Bodrikov, I. V. *Zh. Org. Khim.* **1978**, *14*, 1806.

(9) Kovacic, P.; Bennet, R. P. *J. Am. Chem. Soc.* **1961**, *83*, 221. Symmers, C.; Quin, L. D. *J. Org. Chem.* **1978**, *43*, 1250. Kashman, Y.; Rudi, A. *Tetrahedron Lett.* **1979**, 1077.

(10) Reviews: Smit, W. A.; Zefirov, N. S.; Bodrikov, I. V.; Krimer, M. Z. *Acc. Chem. Res.* **1979**, *12*, 282. Smit, W. A.; Zefirov, N. S.; Bodrikov, I. V. In "IUPAC Organic Sulfur Chemistry", Freidlina, R. Kh., Ed.; Pergamon Press: Oxford, **1981**, 159. Zefirov, N. S.; Koz'min, A. S. In "Soviet Scientific Reviews"; Volpin, M. E., Ed.; Overseas Publishers Association: New York, in press.

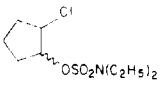
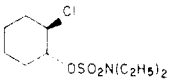
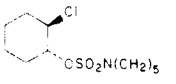
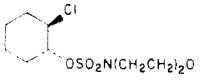
(11) Zefirov, N. S.; Sadovaja, N. K.; Novgorodtseva, L. A.; Achmedova, R. Sh.; Baranov, S. V.; Bodrikov, I. V. *Tetrahedron* **1979**, *35*, 2759.

(12) Zefirov, N. S.; Koz'min, A. S.; Kirin, V. N.; Zhdankin, V. V.; Caple, R. *J. Org. Chem.* **1981**, *46*, 5264.

(13) (a) Potekhin, K. A.; Kurkutova, E. N.; Antipin, M. Yu.; Struchkov, Yu. T.; Maggerramov, A. M.; Sadovaja, N. K.; Zefirov, N. S. *Zh. Org. Khim.* **1977**, *13*, 2093. (b) Gybin, A. S.; Smit, W. A.; Krimer, M. Z.; Zefirov, N. S.; Novgorodtseva, L. A.; Sadovaja, N. K. *Tetrahedron* **1980**, *36*, 1361.

0022-3263/85/1950-4539$01.50/0

Table I. Yields and NMR Data for the SO_3 + R_2NCl Addition Products to Olefins

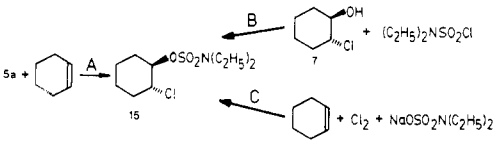
R_2NCl	olefin	adduct	yield, %	^1H NMR, δ, (J, Hz) [^{13}C NMR, ppm]
4a	$CH_2=CH_2$	$CH_2(OSO_2N(C_2H_5)_2)CH_2Cl$ **8**	88	4.10 (t, 2 H, J = 6.0), 3.72 (t, 2 H, J = 6.0) [68.98, 42.89]
4b	$CH_2=CH_2$	$CH_2(OSO_2N(CH_2)_5)CH_2Cl$ **9**	41	4.28 (t, 2 H, J = 6.0), 3.71 (t, 2 H, J = 6.0)
4c	$CH_2=CH_2$	$CH_2(OSO_2N(CH_2CH_2)_2O)CH_2Cl$ **10**	61	4.37 (t, 2 H, J = 5.6), 3.85-3.63 (m, 6 H)
4a	$CH(C_4H_9)=CH_2$	$C_4H_9CH(OSO_2N(C_2H_5)_2)CH_2Cl$ **11**	81	4.68-4.40 (m, 1 H), 3.75-3.60 (m, 2 H) [78.92, 45.34]
4b	$CH(C_4H_9)=CH_2$	$C_4H_9CH(OSO_2N(CH_2)_5)CH_2Cl$ **12**	85	4.72-4.50 (m, 1 H), 3.94-3.58 (m, 2 H)
4c	$CH(C_4H_9)=CH_2$	$C_4H_9CH(OSO_2N(CH_2CH_2)_2O)CH_2Cl$ **13**	70	4.76-4.50 (m, 1 H), 3.96-3.60 (m, 6 H)
4a		 **14**	64	4.89 (m, 1 H), 4.41 (m, 1 H), [87.39, 62.49]
4a		 **15**	85	4.47 (dt, 1 H, $J_1 = J_2 = 7.5$, $J_3 = 4.0$), 4.04 (dt, 1 H, $J_1 = J_2 = 7.5$, $J_3 = 4.0$) [81.79, 59.24]
4b		 **16**	90	4.40 (dt, 1 H, $J_1 = J_2 = 8.2$, $J_3 = 4.5$), 3.94 (dt, 1 H, $J_1 = J_2 = 8.2$, $J_3 = 4.5$)
4c		 **17**	94	4.42 (dt, 1 H, $J_1 = J_2 = 8.0$, $J_3 = 4.4$), 3.96 (dt, 1 H, $J_1 = J_2 = 8.0$, $J_3 = 4.4$)

the presence of added strong electrolytes (e.g., $LiClO_4$).

The fourth approach involves development of new electrophilic reagents, X^+Z^- (or at least strongly polarized ones), with greater reactivity by introducing either Z^- = BF_4^-, SbF_6^-, etc. or Z^- = a strongly nucleofugic group. The supernucleofugic anions such as ClO_4^-, FSO_3^-, and $CF_3SO_3^-$ are particularly useful for this purpose.[2a] In particular, halogen fluorosulfonates[14] and triflates[15] have exceptional halogenation potential.

Recently we have discovered the intriguing phenomenon of covalent binding of nucleofugic anions in carbocationic-like processes.[4a] We demonstrated that the salts of such acids as perchloric, triflic, and fluorosulfonic act as nucleophiles even in the presence of other nucleophilic species.[4a,b,16] As an extension of these studies it occurred to us to develop a novel strategy for the increasing the electrophilicity of certain reagents by inserting SO_3 into the $X^{\delta+}$–$Y^{\delta-}$ bond, leading to new reagents of type **1** (Scheme I). Because of the nucleofugic property of YSO_2O^- anions (even the supernucleofugic FSO_2O^- [4a,17]), one should expect increased polarization in the intermediate reagent **1**; hence one could design novel electrophilic addition processes of types **1** → **2** and **1** → **3**. The crucial point of this approach is the ability of SO_3 to insert into a particular type of X–Y bond. Such insertion of SO_3 has been demonstrated for several types of bonds, e.g., Ac–F,[18] Si–N,[19a] Si–halide,[19a] Si–OSi,[19b] and Cl–halide.[20] This

Scheme II



general synthetic concept has been proved for a number of electrophiles.[21]

The aim of our study was to confirm that SO_3-mediated addition of weak electrophiles to olefins is a useful way of increasing of the effective electrophilicity of these electrophiles because of (i) the ability of SO_3 to act as a Lewis acid and/or (ii) the activation of X–Y species by the "insertion" mechanism (Scheme I). We have chosen as weakly electrophilic reagents the chloroamines R_2NCl because they (i) undergo radical reactions with olefins,[22,23] (ii) fail to react with most alkenes via electrophilic pathways (at least in aprotic, nonpolar solvents[22–24]), and (iii)

(14) Aubke, F.; Gillespie, R. J. *Inorg. Chem.* **1968**, *7*, 599. Fokin, A. V.; Studnev, Yu. N.; Rapkin, A. I.; Tatarinov, A. C. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1916.

(15) Effenberger, F.; Kussmaul, U.; Huthmacher, K. *Chem. Ber.* **1979**, *112*, 1677.

(16) Zefirov, N. S.; Koz'min, A. S.; Yur'eva, N. M.; Zhdankin, V. V.; Kirin, V. N. *Zh. Org. Khim.* **1982**, *18*, 2211. Zefirov, N. S.; Koz'min, A. S.; Sorokin, V. D. *Ibid.* **1982**, *18*, 1768; **1983**, *19*, 876. Zefirov, N. S.; Koz'min, A. S.; Dan'kov, Yu. V.; Zhdankin, V. V.; Kirin, V. N. *Ibid.* **1984**, *20*, 233. Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Yu. V.; Samoshin, V. V.; Koz'min, A. S. *Ibid.* **1984**, *20*, 444.

(17) Kevill, D.; Lin, G. M. *Tetrahedron Lett.* **1978**, 949.

(18) Krespan, C. G.; England, D. C. *J. Org. Chem.* **1975**, *40*, 2937.

(19) (a) Schmidt, M.; Schmidbaur, H. *Angew. Chem.* **1958**, *70*, 657; **1959**, *71*, 384. (b) The insertion of SO_3 into hexamethyldisiloxane has been observed in our lab. (Proskurnina, M. V., unpublished result.)

(20) Paul, R. S.; Arora, C. L.; Malhotra, K. C. *J. Inorg. Nucl. Chem.* **1971**, *33*, 991. Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1970**, *9*, 311. Belaventsev, M. A.; Pashinin, V. A.; Ragulin, L. I.; Sokol'sky, G. A. *Zh. Org. Khim.* **1973**, *9*, 256.

(21) (a) SO_3 + RSCl: Zefirov, N. S.; Koz'min, A. S.; Sorokin, V. D.; Schastin, A. V.; Balenkova, E. S. *Dokl. Akad. Nauk SSSR* **1984**, *276*, 1139. (b) SO_3 + RONO: Zefirov, N. S.; Zyk, N. V.; Kutateladze, A. G. *Zh. Org. Khim.* **1984**, *20*, 5473. (c) SO_3 + Cl_2: Zefirov, N. S.; Koz'min, A. S.; Sorokin, V. D. *J. Org. Chem.* **1984**, *49*, 4086. (d) SO_3 + AcF: Schastin, A. V.; Sorokin, V. D.; Balenkova, E. S.; Koz'min, A. S.; Zefirov, N. S. "XVI Meeting on Chemistry and Technology of Organic Compounds of Sulfur and Sulfurated Petrols"; Riga: Theses, 1984; p 160. (e) SO_3 + RSSR: Sorokin, V. D.; Schastin, A. V.; Balenkova, E. S.; Koz'min, A. S.; Zefirov, N. S. In ref 21d, p 42. (f) SO_3 + $RSNR_2'$: Zefirov, N. S.; Zyk, N. V.; Kutateladze, A. G.; Kolbasenko, S. I.; Lapin, Yu. A. *Zh. Org. Khim.*, in press.

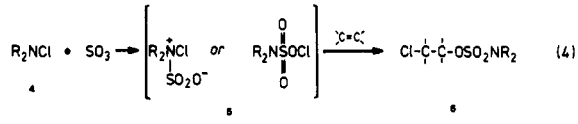
(22) Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* **1970**, *70*, 639. Davies, D. I.; Parrott, M. J. "Free Radicals in Organic Synthesis"; Springer-Verlag: Berlin, 1978; Chapter 9.

(23) Lessard, J.; Couture, Y.; Mondon, M.; Touchard, D. *Can. J. Chem.* **1984**, *62*, 105 and references therein.

promote ionic pathways by Lewis acid catalysis.[25] Thus, they are a good model to establish the usefulness of SO_3-mediated additions to olefins.[26]

Results

We have found that *N*,*N*-diethylchloroamine (**4a**), *N*-chloropiperidine (**4b**), and *N*-chloromorpholine (**4c**) react exothermically with equimolar amounts of SO_3 at −70 to −50 °C in CH_2Cl_2[27] and then with olefins (at −60 °C, allowing the temperature to rise to 20 °C) to give dialkylsulfamates of the corresponding chlorohydrins (**6**, eq 4).



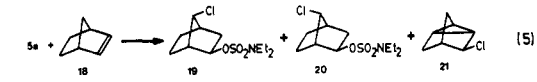
(4)

a R = C_2H_5; b R,R = $(CH_2)_5$; c R,R = $O(CH_2CH_2)_2$;

In most cases the adducts **6** could be easily isolated and purified; the data for these reactions and the ^1H NMR peaks of the adducts are shown in Table I. The addition products **6** were also characterized by spectral and elemental analysis. The structure of adduct **15** from cyclohexene was confirmed by independent synthesis by (i) *reaction of trans-chlorocyclohexanol* (**7**) with $ClSO_2NEt_2$[28] and (ii) chlorination of cyclohexene in the presence of Et_2NSO_2ONa[29] (Scheme II). It should be noted that pathway C of Scheme II is a novel manifestation of the phenomenon of competitive covalent binding of a nucleofugic anion in carbocationic-like processes,[4a] including Ad_E additions[4b,12] (vide supra).

These data demonstrate the general sequence of Scheme I. The yields of the adducts **6** are in many cases high enough to give the reaction synthetic utility, especially since yields were not optimized. Moreover, the data clearly demonstrate the electrophilic nature of the transient reagents **5**. The reaction with 1-hexene proceeds exclusively in accordance with the Markovnikov rule (Table I, adducts **11**–**13**). The addition to cyclohexene proceeds stereospecifically to give trans adducts **15**–**17**. Thus the stereoselectivity and regioselectivity of the additions fit the usual mechanistic picture for Ad_E additions.[1]

Norbornene (**18**) is a typical strained olefin that has been widely used for studies rearrangements in electrophilic additions,[1,8,11] and it has permitted us to evaluate the effective electrophilicity of the reagents by evaluating rearrangement pathways typical for the intermediacy of carbocationic-like species.[7,11] The reaction of norbornene with **5a** gives predominantly the rearranged adduct **19** with synexo configuration of the substituents (eq 5). In addition, we isolated a minor amount of the rearranged adduct **20** with antiexo configuration. Evidently the adduct

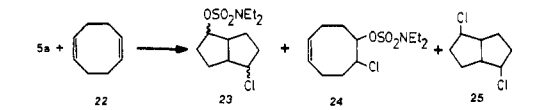


(5)

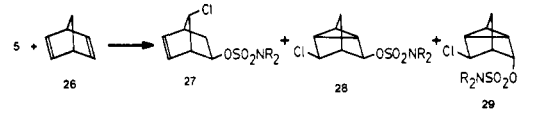
19 is a product of a normal Wagner–Meerwein rearrangement, while the formation of **20** is due to Wagner–Meerwein rearrangement followed by a 1–6 hydride shift. Many analogous processes have been documented in the literature.[8,11,13a,30] Thus the electrophilic character of the reagents **5** is sufficient to cause a rearrangement pathway typical of carbocationic-like intermediates.

It is of interest that we were able to isolate a third product, 3-chloronortricyclene (**21**) (6% yield, eq 5). There are a few examples of the formation of monosubstituted nortricyclenes in electrophilic additions to norbornene,[11,31] but the factors determining this pathway are not yet understood.

Consider now the addition to dienes **22** (eq 6) and **26** (eq 7). Transannular ring closure to give bicyclo[3.3.0]-octanes is a common feature of electrophilic additions to cyclooctadiene (**22**).[8,32] We have found that the addition



(6)



(7)

a R = R = C_2H_5 b R,R = $(CH_2)_5$

of **5a** to **22** in a 1:1 ratio gives a mixture of stereoisomeric 2,6-disubstituted bicyclo[3.3.0]octanes (**23**), the normal adduct **24**, and the byproduct dichloride **25**. Thus the addition to diene **22** also fits the electrophilic mechanism of the process: The effective electrophilicity of the reagents **5** is sufficient to give not only the normal 1,2-adduct but also products of the participation of the second double bond, which is a typical pathway for the addition of effectively strong electrophiles.

The addition of **5a** and **5b** to norbornadiene (**26**) in 1:1 ratio gives a mixture of three compounds **27**, **28**, and **29**. The adduct **27** is the product of a Wagner–Meerwein rearrangement without participation of the second double bond. Products **28** and **29** have the nortricyclene skeleton and hence result from involvement of the homoallylic double bond. The attack by the $R_2NSO_2O^-$ counteranion in the final step of the electrophilic addition proceeds nonstereospecifically to give both epimeric adducts **28** and **29** (for analogous additions to norbornadiene see ref 33). The assignment of configuration in 3,5-disubstituted nortricyclenes is not a simple matter.[33,34] Recently we have

(24) See also: Gassman, P. G. *Acc. Chem. Res.* **1970**, *3*, 26. Gassman, P. G.; Uneyama, K.; Hahnfeld, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 647. Furstoss, R.; Esposito, G.; Teissier, P.; Waegell, B. *Bull. Soc. Chim. Fr.* **1974**, 2485. Wolf, M. E. *Chem. Rev.* **1963**, *63*, 55.

(25) (a) Interaction of Lewis acid with a chloroamine can produce both an aminating agent (attack at a lone pair of chlorine) and a chlorinating agent (attack at the nitrogen lone pair).[2a,24b] (b) Bock, H.; Kompa, K. L. *Chem. Ber.* **1966**, *99*, 1347.

(26) For a preliminary communication, see: Zefirov, N. S.; Zyk, N. V.; Kolbasenko, S. I.; Kutateladze, A. G. *Sulfur Lett.* **1984**, *2*, 95.

(27) The problem of isolation and structural assignment of intermediates **5** is out of the limit of the present paper. For solid **5c** at low temperature the ^{35}Cl NQR spectrum exhibited a signal at 55.63 MHz (data of G. K. Semin and co-workers) which is in the range for alkyl hypochlorites.[21c] However, in the absence of comparative data for complexes of chloroamines with Lewis acids we arbitrarily presented two possible structures in eq 4.

(28) Binkley, W. W.; Degering, E. F. *J. Am. Chem. Soc.* **1939**, *61*, 3250.

(29) (a) Audriech, L. F.; Sveda, M. *J. Org. Chem.* **1944**, *9*, 91. (b) We warmly thank Dr. M. V. Proskurnina for the performance of this experiment.

(30) Borisenko, A. A.; Nikulin, A. V.; Wolfe, S.; Zefirov, N. S.; Zyk, N. V. *J. Am. Chem. Soc.* **1984**, *106*, 1074.

(31) (a) Kwart, H.; Miller, R. K. *J. Am. Chem. Soc.* **1956**, *78*, 5678. (b) Chlorination of norbornene with cross-linked poly(aryl iododichloride) gave especially an appreciable amount (52%) of chloronortricyclene;[31c] the addition of PhI(OH)OTs to norbornene gave 35% of (tosyloxy)nortricyclene.[31d] (c) Šket, B.; Zupan, M.; Zupet, P. *Tetrahedron* **1984**, *40*, 1603. (d) Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Yu. V.; Semerikov, V. N.; Koz'min, A. S. *Zh. Org. Khim.*, in press.

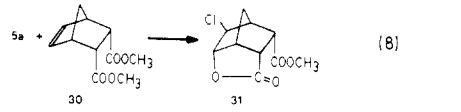
(32) (a) Uemura, S.; Fukuzawa, S.; Toshimitsu, A.; Okano, M.; Tezuka, H.; Sawada, S. *J. Org. Chem.* **1983**, *48*, 270. (b) Osawa, E.; Aigami, K.; Inamoto, Y. *Tetrahedron* **1978**, *34*, 509. (c) Uemura, S.; Onoe, A.; Okano, M. *Bull. Soc. Chim. Jpn.* **1977**, *50*, 1078.

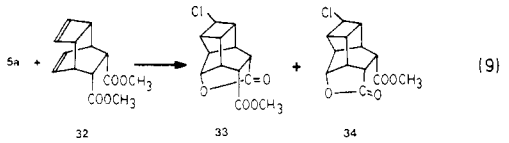
(33) (a) Zefirov, N. S.; Sadovaja, N. K.; Achmedova, R. Sh.; Bodrikov, I. V.; Morrill, T. C.; Nersisyan, A. M.; Rybakov, W. B.; Saraceno, N. D.; Struchkov, Yu. T. *Zh. Org. Khim.* **1980**, *16*, 580. (b) Chizhov, A. O.; Morrill, T. C.; Zefirov, N. S.; Zyk, N. V., submitted for publication. (c) Zefirov,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

(34) Zyk, N. V.; Nikulin, A. V.; Kolbasenko, S. I.; Zefirov, N. S. *Zh. Org. Khim.* **1984**, *20*, 2063. Sadovaja, N. K.; Velikokhat'ko, T. N.; Zefirov, N. S. *Ibid.* **1983**, *19*, 241. Zefirov, N. S.; Sadovaja, N. K.; Velikokhat'ko, T. N.; Andreeva, L. A.; Morrill, T. C. *J. Org. Chem.* **1982**, *47*, 1468.

developed (in collaboration with T. Morrill[33b]) an additive scheme for calculating ^1H and ^{13}C chemical shifts in these systems, which permitted unambiguous assignment of configuration; these data were used in the present paper.

From reactions of diesters **30** and **32** (eq 8 and 9) we isolated only the corresponding chlorolactones **31** and **33** and **34**. In these reactions one of the carbomethoxy groups acts as an internal nucleophile in the final step of the addition, successfully competing with external nucleophilic species. This pathway has many precedents in the literature.[35,36] It is of interest that the addition to diester **32** gave two lactones **33** and **34**.[35b,36] The usual products in this type of reaction are cage δ-lactones of type **33**, which are usually more stable than the corresponding γ-lactones.[32b,36] Accordingly the interrelation of δ- vs. γ-lactones for this cage system is worth special investigation.[32b,35b,36]





Discussion

The results of this study show that the $R_2NCl + SO_3$ addition to a C=C bond is a new electrophilic Ad_E reaction of general character. Moreover, the concept of SO_3-mediated addition of electrophiles to olefins has been confirmed.

Let us emphasize some aspects of this reaction. First, while the starting reagents R_2NCl exhibit preferentially homolytic reactivity,[22,23] the novel transient reagents **5** exhibit electrophilic reactivity. The additions follow Markovnikov regioselectivity and proceed trans stereospecifically, which are characteristic of the electrophilic mechanism of the addition. Moreover, the skeletal rearrangements and homoallylic participation of the second double bond are typical of a carbocationic-like pathway.

Second, the $SO_3 + R_2NCl$ addition offers a practical synthesis of esters of sulfamic acids.[37] The reactions provide access to a new type of 1,2-disubstituted ethanes, the reagents are readily available, and the process is efficient. Moreover, the reagents of type **5** can evidently be used not only for Ad_E reactions but also as chlorinating agents for other synthetic purposes.[27]

The SO_3-mediated transformation of electrophiles can be considered as a promising way to involve other reagents that contain a "weak" X–Y bond in synthetically useful reactions.[38] Further work is in progress to achieve this goal as well as to assess the nature of SO_3 complexes with electrophiles.[21c,27]

Experimental Section

NMR spectra were obtained in $CDCl_3$ (unless otherwise stated) with Tesla BS-497, Varian ST-60, and CFT-20 spectrometers. Me_4Si was used as an internal standard and the chemical shifts are reported in δ units. Commercially obtained CH_2Cl_2 was distilled over P_2O_5. The chloroamines **4a**, **4b**, and **4c** were prepared according to the literature.[25b] All reactions were followed by TLC on Silufol plates (Kavalier, Czechoslovakia). Preparative column chromatography involved silica gel and hexane–AcOEt mixtures as the eluent.

General Procedure. A dry three-necked flask fitted with addition funnel, stirrer, and nitrogen inlet was charged with a solution of chloroamine (5–80 mmol) in CH_2Cl_2. The mixture was cooled to −60 °C, and a precooled solution of an equimolar amount of SO_3 in CH_2Cl_2 was added dropwise, while the temperature was maintained below −50 °C (strong exothermic reaction). The resulting mixture, which was a clear solution in the case of **4a** or a milklike suspension in the case of **4b** and **4c**, was stirred 0.5 h at −40 °C and cooled again to −60 °C, and a solution of an equimolar amount of olefin in CH_2Cl_2 was added dropwise at this temperature. The reaction mixture became homogeneous. In the reaction with ethylene, it was bubbled through the inlet into the mixture at room temperature to saturation.

The workup involved stirring for 0.5 h at room temperature, treatment with a solution of $NaHCO_3$, extraction with $CHCl_3$, and drying over $MgSO_4$. After rotary evaporation of the solvent the crude adduct was either chromatographed or distilled in vacuo.

Reactions of Ethylene. (A) **4a** (0.68 g, 6.27 mmol) in 3 mL of CH_2Cl_2 and 0.5 g (6.27 mmol) of SO_3 gave 1.2 g (88%) of 2-chloroethyl *N,N*-diethylsulfamate (**8**); bp 95–96 °C (1 mm); n^{18}_D 1.4580. Anal. Calcd for $C_6H_{14}ClNO_3S$: C, 33.41; H, 6.54; Cl, 16.44; N, 6.49; S, 14.86. Found: C, 33.39; H, 6.53; Cl, 16.39; N, 6.20; S, 14.60. (B) **4b** (2.57 g, 21.5 mmol) in 10 mL of CH_2Cl_2 and 1.72 g of SO_3 in 15 mL of CH_2Cl_2 gave 2.1 g (41%) of 2-chloroethyl 1-piperidinesulfonate (**9**) by chromatography (4:1 hexane–AcOEt): n^{21}_D 1.4725. Anal. Calcd for $C_7H_{14}ClNO_3S$: C, 36.92; H, 6.20; N, 6.15. Found: C, 37.22; H, 6.36; N, 6.35. (C) **4c** (4.45 g, 36.6 mmol) in 20 mL of CH_2Cl_2 and 2.93 g of SO_3 in 15 mL of CH_2Cl_2 gave 5.15 g (61%) of 2-chloroethyl 4-morpholinesulfonate (**10**) by chromatography (3:1 hexane–AcOEt): n^{23}_D 1.4745. Anal. Calcd for $C_6H_{12}ClNO_4S$: C, 31.38; H, 5.27; N, 6.10. Found: C, 31.50; H, 5.03; N, 6.38.

Reactions of Hexene-1. (A) From 2.4 g (22.1 mmol) of **4a** in 10 mL of CH_2Cl_2, 1.77 g of SO_3 in 9 mL of CH_2Cl_2, and 1.86 g of hexene in 10 mL of CH_2Cl_2 was obtained 4.88 g (81%) of 1-chloro-2-hexyl *N,N*-diethylsulfamate (**11**): bp 102–104 °C (2 mm); n^{20}_D 1.4574. Anal. Calcd for $C_{10}H_{22}ClNO_3S$: C, 44.19; H, 8.16; Cl, 13.04; N, 5.15; S, 11.80. Found: C, 44.36; H, 8.09; Cl, 13.20; N, 5.15; S, 11.46. (B) From 1.48 g (12.4 mmol) of **4b** in 10 mL of CH_2Cl_2, 0.99 g of SO_3 in 10 mL of CH_2Cl_2, and 1 g of 1-hexene in 10 mL of CH_2Cl_2 was obtained 3.01 g (85%) of 1-chloro-2-hexyl *N*-piperidinylsulfonate (**12**): bp 156 °C (1 mm); n^{19}_D 1.4753. Anal Calcd for $C_{11}H_{22}ClNO_3S$: C, 46.55; H, 7.81; N, 4.94. Found: C, 46.76; H, 7.65; N, 4.89. (C) From 2.65 g (21.8 mmol) of **4c** in 10 mL of CH_2Cl_2, 1.74 g of SO_3 in 10 mL of CH_2Cl_2, and 1.83 g of 1-hexene in 10 mL of CH_2Cl_2 was obtained 4.35 g (70%) of 1-chloro-2-hexyl *N*-morpholinosulfonate (**13**) by chromatography (7:1 hexane–AcOEt): n^{22}_D 1.4731. Anal. Calcd for $C_{10}H_{20}ClNO_4S$: C, 42.03; H, 7.05; N, 4.90; S, 11.22. Found: C, 42.07; H, 6.80; N, 4.75; S, 10.96.

Reactions of Cyclohexene. (A) From 1.05 g (9.8 mmol) of **4a** in 30 mL of CH_2Cl_2, 0.78 g of SO_3 in 6 mL of CH_2Cl_2, and 0.8 g of cyclohexene in 10 mL of CH_2Cl_2 was obtained 2.24 g of *trans*-2-chlorocyclohexyl *N,N*-diethylsulfamate (**15**): R_f 0.76 (silica gel, 6:1 hexane–AcOEt); bp 62–63 °C (1 mm); n^{21}_D 1.4775; mass spectrum, *m/e* 269, 271. Anal. Calcd for $C_{10}H_{20}ClNO_3S$: C, 44.52; H, 7.47; Cl, 13.14; N, 5.19; S, 11.88. Found: C, 44.66; H, 7.54; Cl, 12.94; N, 5.19; S, 11.70. (B) From 1.05 g (8.8 mmol) of **4b** in 10 mL of CH_2Cl_2, 0.7 g of SO_3 in 10 mL of CH_2Cl_2, and 0.72 g of cyclohexene in 10 mL of CH_2Cl_2 was obtained 2.23 g of *trans*-2-chlorocyclohexyl 1-piperidinesulfonate (**16**): bp 155 °C (1 mm); n^{20}_D 1.5018. Anal. Calcd for $C_{11}H_{20}ClNO_3S$: C, 46.88;

(35) (a) Ver Nooy, Ch. D.; Rondestvedt, C. S. *J. Am. Chem. Soc.* **1955**, *77*, 3583. (b) Garratt, D. G.; Ryan, M. D.; Beaulieu, P. L. *J. Org. Chem.* **1978**, *45*, 839.

(36) (a) Zefirov, N. S.; Kirin, V. N.; Koz'min, A. S.; Krimer, M. Z. *Zh. Org. Khim.* **1981**, *17*, 13. (b) Zefirov, N. S.; Kirin, V. N.; Koz'min, A. S.; Bodrikov, I. V.; Potekhin, K. A.; Kurkutova, E. N. *Tetrahedron Lett.* **1978**, 2617. (c) Kondo, A.; Yamane, T.; Ashida, T.; Sasaki, T.; Kanematsu, K. *J. Org. Chem.* **1978**, *43*, 1180.

(37) Dorlars, A. In "Methoden der Organischen Chemie (Houben-Weyl)"; Müller, E., Ed.; Thieme Verlag: Stuttgart, 1958; Vol. 11, Part 2, Chapter 5.

(38) Fluorodialkylamines[39] seem to be a promising candidates taking into account the stability and strong nucleofugic property of FSO_3^- anion.[17] The insertion of SO_3 (and subsequent reactions) into a variety of "weak" bonds including ROOR', R_2NNR_2, etc. is actively under way in our lab.

(39) Wiesboeck, R. A.; Ruff, J. K. *Inorg. Chem.* **1966**, *5*, 1629. Banks, R. E.; Haszeldine, R. N.; Hatton, R. *Tetrahedron Lett.* **1967**, *41*, 3993. Gupta, O. D.; Shreeve, J. M. *J. Chem. Soc., Chem. Commun.* **1984**, 416.

H, 7.15; N, 4.97. Found: C, 47.18; H, 7.26; N, 5.35. (C) From 3.55 g (29.2 mmol) of **4c** in 10 mL of CH_2Cl_2, 2.34 g of SO_3 in 10 mL of CH_2Cl_2, and 2.4 g of cyclohexene in 10 mL of CH_2Cl_2 was obtained 7.78 g of *trans*-chlorocyclohexyl 4-morpholinesulfonate (**17**) by chromatography (7:1 hexane–AcOEt): n^{21}_D 1.4988. Anal. Calcd for $C_{10}H_{18}ClNO_4S$: C, 42.33; H, 6.39; N, 4.94. Found: C, 42.32; H, 6.31; N, 4.98.

Alternative Syntheses of 15. (A) A mixture of 4.2 g of **7** with 3.14 g of triethylamine was added to a stirred solution of Et_2NSO_2Cl[28] (5.32 g) in 20 mL of hexane, and the resulting mixture was refluxed for 10 h. The usual workup and distillation in vacuo gave 1.1 g (10%) of **15** identical with the above sample. (B)[29b] A slight excess of chlorine was bubbled into a stirred mixture of Et_2NSO_3Na (3.3 g) and cyclohexene (1.5 g) in 30 mL of AcOEt at −65 °C, and the usual workup and chromatography (9:1 hexane–AcOEt) gave 1.17 g (24%) of **15**.

Reaction of Cyclopentene with 4a. From 8.28 g (77 mmol) of **4a** in 30 mL of CH_2Cl_2, 6.16 g of SO_3 in 20 mL of CH_2Cl_2, and 5.24 g of cyclopentene in 20 mL of CH_2Cl_2 was obtained 12.6 g of 2-chlorocyclopentyl *N,N*-diethylsulfamate (**14**): bp 125 °C (3 mm); n^{21}_D 1.4680. Anal. Calcd for $C_9H_{18}ClNO_3S$: C, 42.27; H, 7.09; Cl, 13.86; N, 5.48; S, 12.54. Found: C, 42.07; H, 6.51; Cl, 13.83; N, 5.02; S, 12.54.

Reaction of Norbornene with 4a. From 1.79 g of **4a** in 10 mL of CH_2Cl_2, 1.33 g of SO_3 in 8 mL of CH_2Cl_2, and 1.53 g (16.3 mmol) of norbornene in 10 mL of CH_2Cl_2 was obtained 4.6 g of yellow oil. The chromatography on silica gel (6:1 hexane–AcOEt) gave the following fractions. (a) **21**:[40] 0.14 g (6.0%); ^1H NMR (CCl_4) 3.83 (m, 1 H, HCCl), 2.20–1.90 (m, 2 H), 1.53–1.20 (m, 6 H); ^{13}C NMR 65.10 (CCl), 37.04, 31.48, 30.12, 17.44, 13.64, 11.10. (b) *anti*-7-Chloro-*exo*-bicyclo[2.2.1]heptan-2-yl *N,N*-diethylsulfamate (**20**): 0.66 g (14%); R_f 0.39; bp 93 °C (1 mm); n^{19}_D 1.4923; ^1H NMR (CCl_4) 4.49 (dd, 1 H, J = 3.5 Hz, J_2 = 7 Hz, HCO), 4.10 (s, 1 H, HCCl), 3.22 (q, 4 H, NCH_2), 2.62 and 2.32 (2 m, 1 H each), 2.08–1.80 (m, 6 H), 1.19 (t, CH_3); ^{13}C NMR 81.15 (CO), 63.08 (CCl), 48.33 (CH_2N), 42.76, 41.38, 38.07, 25.29, 21.66, 13.37 (CH_3). Anal. Calcd for $C_{11}H_{20}ClNO_3S$: C, 46.88; H, 7.15; Cl, 12.58; N, 4.97; S, 11.38. Found: C, 46.75; H, 6.83; Cl, 12.86; N, 4.72; S, 10.87. (c) *syn*-7-Chloro-*exo*-bicyclo[2.2.1]heptan-2-yl *N,N*-diethylsulfamate (**19**): 2.85 g (62% yield); R_f 0.30; bp 93 °C (1 mm); n^{19}_D 1.4920; ^1H NMR 4.49 (octet, 1 H, J_1 = 7 Hz, J_2 = 3.5 Hz, J_3 = 1 Hz, HCO), 3.92 (s, 1 H, HCCl), 3.26 (q, 4 H, NCH_2), 2.64 and 2.39 (2 m, 1 H each), 2.22–1.56 (m, 6 H), 1.18 (t, 6 H, CH_3); ^{13}C NMR 81.35 (CO), 63.26 (CCl), 47.09 (CH_3), 42.32, 42.21, 37.39, 25.27, 23.67, 13.06 (CH_3). Anal. Calcd for $C_{11}H_{20}ClNO_3S$: C, 46.88; H, 7.15; Cl, 12.58; N, 4.97; S, 11.38. Found: C, 46.67; H, 6.69; Cl, 12.78; N, 4.74; S, 11.00.

Reaction of Cycloocta-1,5-diene (22) with 4a. From 4.28 g (39.8 mmol) of **4a** in 25 mL of CH_2Cl_2, 3.19 g of SO_3 in 25 mL of CH_2Cl_2, and 4.3 g of cyclooctadiene in 20 mL of CH_2Cl_2 was obtained 11.2 g of yellow oil. Chromatography on silica gel (9:1 hexane–AcOEt) gave the following fractions. (a) **25**: 2.46 g (34%); mp 41 °C; ^1H NMR spectrum is in accordance with the literature data.[32] (b) 6-Chloro-1-cycloocten-5-yl *N,N*-diethylsulfamate (**24**): 2.7 g (23%); R_f 0.45; n^{21}_D 1.4945; ^1H NMR 5.72–5.44 (m, 2 H, =CH), 4.80–4.40 (m, 1 H, HCO), 4.40–4.02 (m, 1 H, HCCl), 3.14 (q, 4 H, CH_2), 2.70–1.80 (m, 8 H), 1.14 (t, 6 H, CH_3); ^{13}C NMR 129.54 and 127.82 (=C), 84.37 (CO), 62.29 (CCl); IR 3013 (H—C=), 1648 (C=C) cm^{-1}. Anal. Calcd for $C_{12}H_{22}ClNO_3S$: C, 48.72; H, 7.50; N, 4.73. Found: C, 49.06; H, 6.97; N, 5.01. (c) 6-Chlorobicyclo[3.3.0]octan-2-yl *N,N*-diethylsulfamate (**23**): 2.08 g (18%); R_f 0.3; n^{21}_D 1.4728; ^1H NMR 4.88–4.28 (m, 2 H, overlapping signals of HCO and HCCl), 3.32 (q, 4 H, CH_2N), 2.44–1.98 (m, 10 H), 1.26 (t, 6 H, CH_3); ^{13}C NMR 81.94 (CO), 61.78 (CCl). Anal Calcd for $C_{12}H_{22}ClNO_3S$: C, 48.72; H, 7.50; Cl, 11.98; N, 4.73; S, 10.84. Found: C, 48.09; H, 7.70; Cl, 12.05; N, 4.97; S, 10.90. (d) Three other isomers (1.91 g, 16%) of **23** were obtained (TLC data) for which ^1H NMR and elemental analyses were identical to those of the sample of entry c.

Reactions of Norbornadiene (26). (A) From 4.56 g (42.4 mmol) of **4a** in 20 mL of CH_2Cl_2, 3.4 g of SO_3 in 20 mL of CH_2Cl_2, and 3.9 g of norbornadiene in 20 mL of CH_2Cl_2 was obtained 11.3 g of brown oil. Chromatography on silica gel (benzene) gave the following fractions. (a) *syn*-7-Chloro-2-bicyclo[2.2.1]hepten-*exo*-6-yl *N,N*-diethylsulfamate (**27a**): 2.8 g (24%); R_f 0.43; n^{20}_D 1.4960; ^1H NMR (CCl_4) 6.24 (octet, 1 H, J_1 = 6.5 Hz, J_2 = 3.5 Hz, J_3 = 1.1 Hz, HC=), 6.09 (octet, 1 H, J_1 = 6.5 Hz, J_2 = 3.8 Hz, J_3 = 1.8 Hz, HC=), 4.46 (octet, 1 H, J_1 = 7.5 Hz, J_2 = 3.5 Hz, J_3 = 1.8 Hz, HCO), 3.98 (dd, 1 H, J_1 = 2.8 Hz, J_2 = 1.5 Hz, HCCl), 3.28 (q, 4 H, CH_2N), 2.88 and 2.38–2.04 (2 m, 1 H each), 1.99 and 1.75 (2 m, 1 H each), 1.16 (t, 6 H, CH_3). Anal. Calcd for $C_{11}H_{18}ClNO_3S$: C, 47.22; H, 6.48; Cl, 12.67; N, 5.01; S, 11.46. Found: C, 47.57; H, 6.74; Cl, 12.62; N, 5.40; S, 11.41. (b) *exo*-5-Chloro-*endo*-nortricyclen-3-yl *N,N*-diethylsulfamate (**29a**): 5.46 g (46%); R_f 0.37; n^{21}_D 1.4910; ^1H NMR (CCl_4) 4.53 (s, 1 H, HCCl), 4.37 (s, 1 H, HCO), 3.24 (q, 4 H, CH_2N), 2.48–1.92 (m, 3 H), 1.64 (m, 3 H), 1.19 (t, 6 H, CH_3). Anal Calcd for $C_{11}H_{18}ClNO_3S$: C, 47.22; H, 6.48; N, 5.01. Found: C, 47.34; H, 6.71; N, 4.88. (c) *exo*-5-Chloro-*exo*-nortricyclen-3-yl *N,N*-diethylsulfamate (**28a**): 2.86 g (24%); R_f 0.3; n^{21}_D 1.4916; ^1H NMR (CCl_4) 4.34 (s, 1 H, HCO), 3.88 (s, 1 H, HCCl), 3.18 (q, 4 H, CH N), 2.44–1.90 (m, 3 H), 1.60 (m, 3 H), 1.14 (t, 6 H, CH_3). Anal. Calcd for $C_{11}H_{18}ClNO_3S$: C, 47.22; H, 6.48; Cl, 12.67; N, 5.01; S, 11.46. Found: C, 47.29; H, 6.70; Cl, 12.40; N, 5.23; S, 11.29. (B) From 3.58 g (29.9 mmol) of **4b** in 12 mL of CH_2Cl_2, 2.39 g of SO_3 in 12 mL of CH_2Cl_2, and 2.75 g of norrbornadiene in 15 mL of CH_2Cl_2 was obtained 8.46 g of yellow oil. Chromatography on silica gel (1:4 benzene–hexane) gave the following fractions. (a) *exo*-5-Chloro-*endo*-nortricyclen-3-yl 1-piperidinesulfonate (**29b**): 2.44 g (28%); R_f 0.35; n^{25}_D 1.5065; ^1H NMR (CD_2Cl_2) 4.64 (s, 1 H, HCCl), 4.46 (s, 1 H, HCO), 3.34–3.12 (m, 4 H, CH_2N), 2.34–1.54 (m, 14 H). Anal. Calcd for $C_{12}H_{18}ClNO_3S$: C, 49.40; H, 6.22; N, 4.80. Found: C, 49.76; H, 6.18; N, 4.85. (b) A 1:1 mixture of **28b** + **29b**: 3.95 g (45%) ^1H NMR [*exo*-5-chloro-*exo*-nortricyclen-3-yl 1-piperidinesulfonate (**28b**)] 4.44 (s, 1 H, HCO), 3.96 (s, 1 H, HCCl). Anal. Calcd for $C_{12}H_{18}ClNO_3S$: C, 49.40; H, 6.22; N, 4.80. Found: C, 49.58; H, 6.02; N, 4.85. (c) *syn*-7-Chloro-2-bicyclo-[2.2.1]hepten-*exo*-6-yl 1-piperidinesulfonate (**27b**): 1.3 g (15%); R_f 0.23; n^{25}_D 1.5118; ^1H NMR (CD_2Cl_2) 6.24 and 6.05 (2 octets, 1 H each, J_1 = 6.5 Hz, J_2 = 3.0 Hz, J_3 = 1.0 Hz, HC=), 4.55 (dd, 1 H, J_1 = 7.8 Hz, J_2 = 3.5 Hz, HCO), 4.06 (br s, 1 H, HCCl), 3.26 (m, 4 H, CH_2N), 2.96–1.68 (m, 10 H). Anal. Calcd for $C_{12}H_{18}ClNO_3S$: C, 49.40; H, 6.22; N, 4.80. Found: C, 49.76; H, 6.18; N, 4.85.

Reaction of Diester 30 with 4a. From 7.1 g (66 mmol) of **4a** in 20 mL of CH_2Cl_2, 5.28 g of SO_3 in 20 mL of CH_2Cl_2, and 13.9 g of the diester **30** in 25 mL of CH_2Cl_2 was obtained 14.4 g (95%) of 2-chloro-8-carbomethoxy-4-oxatricyclo[5.1.1^{1,6}0^{3,7}]nonan-5-one (**31**): mp 64–65 °C (from pentane); IR 1790, 1730 cm^{-1}; ^1H NMR 4.80 (d, 1 H, J = 5.0 Hz, HC–O), 4.56 (d, 1 H, J = 2 Hz, HCCl), 3.72 (s, 3 H, CH_3O), 3.46–2.76 (m, 3 H), 2.42–2.22 (m, 1 H), 1.74–1.30 (m, 2 H). Anal. Calcd for $C_{10}H_{11}ClO_4$: C, 52.08; H, 4.81; Cl, 15.37. Found: C, 51.23; H, 4.84; Cl, 15.64.

Reaction of Diester 32 with 4a. From 0.41 g of **4a** in 5 mL of CH_2Cl_2, 0.3 g of SO_3 in 5 mL of CH_2Cl_2, and 0.94 g (3.8 mmol) of diester **32** in 10 mL of CH_2Cl_2 was obtained 0.92 g (90%) of a 1.5:1 mixture of 4-chloro-9-carbomethoxy-8-hydroxytetracyclo[4.2.2.0^{2,5}0^{3,7}]decane-10-carboxylic acid lactone (**33**) and 4-chloro-10-carbomethoxy-8-hydroxytetracyclo[4.2.2.0^{2,5}0^{3,7}]decane-9-carboxylic acid lactone (**34**) as a crystalline solid: mp 179 °C (from benzene); IR 1788 (C=O of **34**), 1769 (C=O of **33**); ^{13}C NMR contains four types of C=O at 176.67, 172.30, 171.75, 171.23; ^1H NMR contains the peaks of **33** and **34** at 4.8 (dd, 1 H, J_1 = 7.5 Hz, J_2 = 2.0 Hz) and 4.6 (dd, 1 H, J_1 = 7.5 Hz, J_2 = 2.0 Hz). Anal. Calcd for $C_{13}H_{13}ClO_4$: C, 58.11; H, 4.88; Cl, 13.19. Found: C, 58.15; H, 5.11; Cl, 12.77.

Registry No. **4a**, 5775-33-7; **4b**, 2156-71-0; **4c**, 23328-69-0; **7**, 6628-80-4; **8**, 93293-18-6; **9**, 98525-50-9; **10**, 98525-51-0; **11**, 93293-19-7; **12**, 98539-80-1; **13**, 98525-52-1; **14**, 93293-20-0; **15**, 91509-10-3; **16**, 98525-53-2; **17**, 98525-54-3; **19**, 98525-55-4; **20**, 98525-56-5; **21**, 3509-46-4; **22**, 111-78-4; **23**, 98525-59-8; **24**, 98525-58-7; **25**, 98525-57-6; **26**, 121-46-0; **27a**, 98525-60-1; **27b**, 98525-63-4; **28a**, 98575-93-0; **28b**, 98575-94-1; **29a**, 98525-61-2; **29b**, 98525-62-3; **30**, 39589-98-5; **31**, 35242-38-7; **32**, 35211-83-7; **33**, 82480-58-8; **34**, 51425-69-5; SO_3, 7446-11-9; CH_2=CH_2, 74-85-1; $CH(C_4H_9)$=CH_2, 592-41-6; Et_2NSO_2Cl, 20588-68-5; Et_2NSO_3Na, 38611-96-0; cyclopentene, 142-29-0; cyclohexene, 110-83-8; norbornene, 498-66-8.

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