Electrophilic Addition of Arylsulfenyl Chlorides to Tricyclo[4.2.2.0^{2,5}]deca-3,7-diene and -3,7,9-triene Systems. Novel Skeletal Rearrangements and Serendipitous Products[1]

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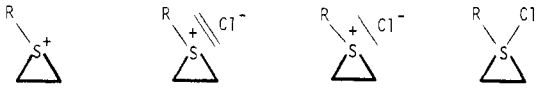
The addition of 2-nitro- and 2,4-dinitrobenzenesulfenyl chlorides in AcOH and under "doping conditions" (AcOH + $LiClO_4$) to the olefins **8–10** has been investigated, and novel types of Wagner–Meerwein rearrangement have been found. The product distributions as well as the different configurations of rearranged chlorides (e.g., **18c**) and acetates (e.g., **18d**) were explained in terms of an ion-pair mechanism. Doping addition leads in part to the formation of covalent perchlorates (e.g., **12d,e**), which have been isolated and identified. The general mechanistic features and stereochemical sequence for the ion-pair mechanism of ArSCl addition to a carbon–carbon double bond are discussed.

The addition of electrophilic agents to the carbon–carbon double bond is one of the most typical processes in organic chemistry. Usually these reactions give *trans*-1,2-adducts, often with the incorporation of external nucleophiles. However, they can also provide a number of other structural types including the products of skeletal rearrangements, proton elimination, etc., all of which are typical reaction paths available to cationoid intermediates.[3] Hence, all electrophilic agents can be divided roughly into strong and weak electrophiles according to their effective electrophilicity which depends on their propensity to follow one of these carbocationic-like pathways. For example, the addition of Cl_2 and Br_2 in polar media often occurs with skeletal rearrangement (e.g., to bicyclic olefins[3,4]) which permits one to classify them as examples of effectively strong electrophiles. In contrast, the additions of HgX_2,[3,5] NOCl,[3,6] and RSCl[3,7-9] proceed mainly without rearrangement, and these reagents are typical of weak electrophiles. The synthetic consequence of this classification is evident: a variety of structures such as the rearranged ones can be obtained only in addition reactions of strong electrophiles, and the problem of increasing the effective electrophilicity of weak electrophiles to obtain these products could be important to a synthetic design.

Since the work of Roberts and Kimball,[10] the concept of a cyclic intermediate onium ion is the most widely accepted one for almost all types of electrophilic addition. A modern MO description of the bonding in these cyclic intermediates, first used by Dewar, suggests a π-complex structure with back-donation.[11] In recent years these cyclic ions have been investigated extensively, both experimentally and theoretically. For example, three-membered-ring episulfonium ion intermediates, **1** (Chart I), have been assumed to exist in the electrophilic addition of sulfenyl chlorides to alkenes for many years.[3,7,8] Recently, these species have been generated by a number of pathways[8] and have been investigated by NMR. Calculations of their electronic structure also have been performed.[11,12]

Chart I



1 **2** **3** **4**

However, this *ionic* representation of the intermediate structues is valid, strictly speaking, only for the addition of ionic complexes as, for example, $(RS)_2SR^+SbCl_6^-$, $NO_2^+BF_4^-$, pure Hal^+ or HgX^+ ions, etc.[13] For the majority of the typically used electrophiles, $X^+\cdots Y^-$ (e.g., Cl_2, RSCl, etc.), it is hard to accept the complete dissociation of the X–Y bond in the intermediates, and hence their structures are better described as *ion pairs* rather than pure ions. The existence of ion-pair intermediates for electrophilic additions have been suggested in a number of investigations;[3,14,15] but their existence is sometimes proposed on purely speculative grounds. For synthetic purposes the difference between the ion pair and ion presentation for the structure of the intermediate seems at first sight too subtle to be important. However recent investigations revealed the remarkable difference and synthetic utility of this mechanistic division.[8]

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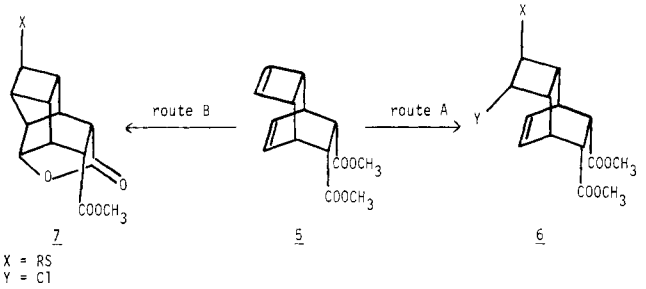
0022-3263/81/1946-5264$01.25/0

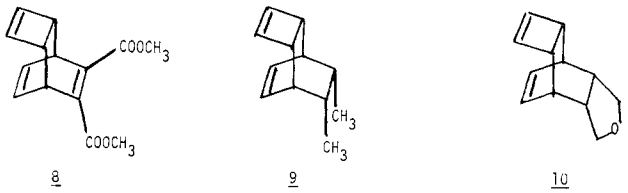
Scheme I



Two of the approaches used for evaluating the relative importance of the ion-pair vs. ion mechanisms are presented below. First of all, the direct comparison of the chemical behavior of specially prepared episulfonium ions[16-18] (ESI's, 1) with the characteristic features of the addition reaction of RSCl to olefins reveales a sharp difference in the course of these processes, a result which must be taken as an argument for involvement of bridged species less polar than an ESI in the RSCl additions.[8] In other words, the real behavior of ESI's, which should in fact be regarded as strong electrophilic species because they are able to take part in all processes usually associated with the formation of cationoid intermediates, has little in common with the more generally recognized weak electrophilic nature of RSCl addition reactions.[8]

Second, it is now recognized that one can change the effective electrophilicity of RSCl by an appropriate change of the reaction conditions.[8,9,18-26] The ESI 1, in fact, represents the limiting case of the intermediate with complete dissociation of the S–Cl bond. A priori, one may assume that a number of species exist with various degrees of polarization of the S–Cl bond. Among them one may distinguish the solvent separated (2) and intimate (3) ion pairs as well as a second limiting structure with a covalent S–Cl bond, namely, the sulfurane 4. Evidently ESI 1 is the most electrophilic of all possible species (1–4). Hence the change of the effective electrophilicity of RSCl with a change in the polarity of media is a crucial test for the involvement of some less polar intermediate.

Chart II



By an effort of our group it was shown first that the use of a solvent with "high ionizing power" (e.g., HCOOH) leads to an increase in the effective electrophilicity of RSCl (judged by the formation of rearranged formates) which is in agreement with the idea of the intermediate formation of ion pairs in these reactions.[27a] Second, we have discovered the occurrence of a "doping effect": substantially increasing the effective electrophilicity of RSCl when the reaction is carried out in the presence of strong electrolytes (usually $LiClO_4$).[8,9,18-26] Exploration of this doping-addition principle has led to important theoretical results because the question of ion-pair intermediates in electrophilic additions could now be treated on an experimental basis[8,19a,26a] (vide supra). Furthermore, it became possible to govern the course of RSCl addition by the choice of proper reaction conditions to obtain products of skeletal rearrangement,[9,19-21] from a series of rearrangements[20,22] involving hydride shifts,[18,20,21] and from a new type of 1,2-addition.[23]

The object of the present investigation was to apply the doping-addition principle to the interaction of RSCl with derivatives of the tricyclo[4.2.2.0^{2,5}]deca-3,7-diene system (for preliminary papers see the references in ref 22). The idea behind this was the fact that previous data was mainly concerned with the addition to the diester 5 and revealed the following regularities: (1) weak electrophiles interact with the strained cyclobutene double bond of diester 5 to give the adduct of type 6[28] (Scheme I, route A); (2) the

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(28) Some cases of the unusual cis addition to tricyclo[4.2.2.0^{2,5}]deca-3,7-diene derivatives (Br_2,[29] PhSCl,[30] PhSeCN,[31] $Hg(OAc)_2$,[32] and IN_3[33]) have been reported, but only for a single case (addition of Br_2[29]) has unambiguous structural proof been presented (X-ray data). However, while the addition of PhSCl to diester 5 has been claimed to give a mixture of cis and trans adducts,[30] we could not reproduce these experimental results, and for every case investigated we obtained only trans adducts of type 6, the structures of which have been unambiguously determined by X-ray diffraction.[34] Analogously, X-ray data showed that the adduct of $Hg(OAc)_2$ to 5 has the transconfiguration with an endo position for the mercury.[35] The problem of configurational assignment by NMR in these structures had been reinvestigated.[34a,b] The exceptional cases of cis addition of RSCl to other olefins have also been discussed.[18a,25]

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Table I. Reactions of Compounds 8-10 with Arenesulfenyl Chlorides under Various Conditions

olefin	ArSCl	temp, °C	solvent	salt	products (yield, %)
8	NBSC	20	AcOH		**11a** (23), **12a** (6), **12b** (41), **13a** (14)
		20	AcOH	$LiClO_4$ [a]	**12b** (40), **13a** (20), **12d** + **12e** (16)
		20	AcOH	$LiBF_4$ [a]	**11a** (4), **12b** (53), **12f** (7), **13a** (23)
		20	CH_3CN		**12g** (52)
		20	CH_3CN	$LiBF_4$ [b]	**12g** (71)
	DNBSC	20	AcOH		**11b** (30), **12h** (52), **13b** (6)
		20	AcOH	$LiClO_4$ [a]	**12h** (47), **13b** (15), **12i** + **12j** (18)
		20	AcOH	$LiClO_4$ [c]	**12h** (36), **12i** + **12j** (27), **14** (22)
9	NBSC	20	AcOH		**17a** (43), **18a** (23), **19a** + **20** (25)
		20	AcOH	$LiClO_4$ [d]	**18a** (43), **18b** (35), **21** (17)
		55	AcOH	$LiClO_4$ [b]	**18a** (21), **21** (20)
	DNBSC	20	AcOH		**17b** (25), **18c** (15), **18d** (30), **19b** + **22** (18)
		20	AcOH	$LiClO_4$ [d]	**18d** (40), **18e** (14)
10	NBSC	20	AcOH		**24a** (35), **25a** (5), **26** (27), **27a** (7)
		20	AcOH	$LiClO_4$ [b]	**25a** (33), **25b** (52)
		55	AcOH	$LiClO_4$ [a]	**25a** (29), **25b** (53)
	DNBSC	20	AcOH		**24b** (16), **25c** (13), **25d** (8), **27b** (34)
		20	AcOH	$LiClO_4$ [a]	**25d** (16), **25e** (53)
		55	AcOH	$LiClO_4$ [a]	**25c** (42), **25d** (19)

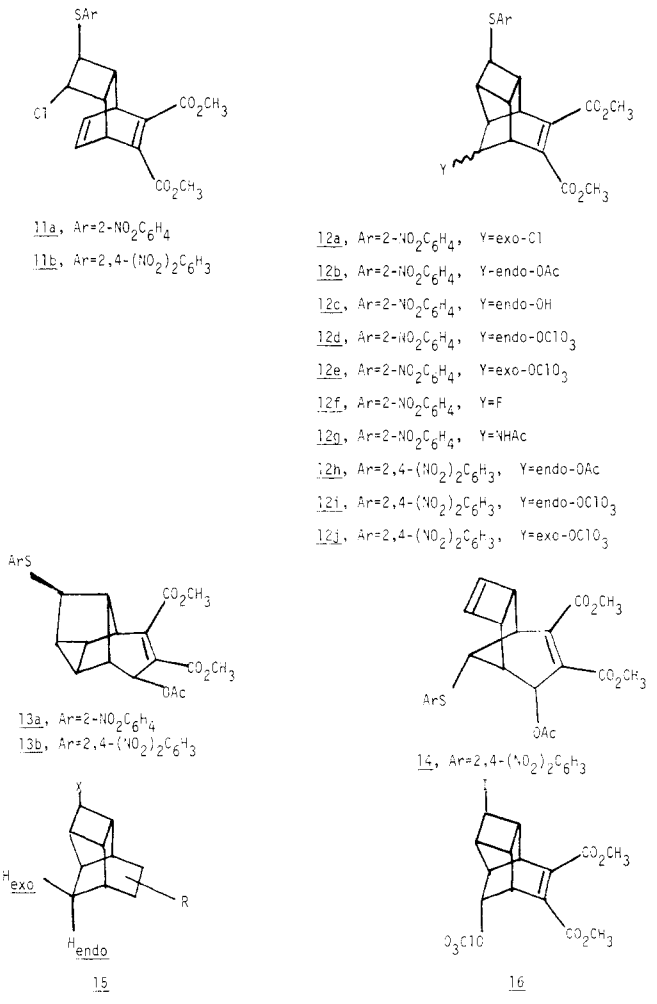
[a] 2 molar equiv. [b] 4 molar equiv. [c] 10 molar equiv. [d] 5 molar equiv.

addition of strong electrophiles involves the cross-type participation of the second carbon–carbon double bond leading to δ-lactone formation (Scheme I, route B).[36] The addition of RSCl obeys these rules: in nonpolar solvents the formation of 1,2-addition products from the cyclobutene double bond has been observed[30,34] in accordance with the weak electrophilic nature of these reagents, but the addition under doping conditions has led to formation of the caged δ-lactone **7** (X = 2-$NO_2C_6H_4S$).[37a] Hence, it was of interest to investigate the doping additions of RSCl to other model compounds of this series where structural features do not permit lactone ring closure and, hence, open the door for other modes of skeletal transformations and the possibility of obtaining other serendipitous products.

Results

Three compounds, namely, triene diester **8** and dienes **9** and **10** (Chart II), have been chosen for the title investigation for several reasons: (1) their accessibility by known synthetic routes;[32b,38] (2) their common structural feature of making route B (Scheme I) impossible for the electrophilic addition; (3) the availability of data regarding the addition of RSCl to these compounds in nonpolar media

Chart III



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(36) Up to 1978 the formation of the five-membered γ-lactone moiety had been reported on the basis of IR absorptions at 1740–1770 cm^{-1}. However, X-ray data obtained by our group[37a] and Sasaki and co-workers[29] revealed the presence of a δ-lactone ring, and all previously published structures need to be revised. This problem has been also analyzed by molecular mechanics method.[37b] For other related publications see ref 37c.

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and the unambiguous proof of the adduct structures.[34]

In the present work we have studied the addition of 2-nitrobenzenesulfenyl (NBSC) and 2,4-dinitrobenzenesulfenyl (DNBSC) chlorides to the olefins **8–10** in polar media (CH_3COOH and CH_3CN) and under doping-addition conditions (CH_3COOH + $LiClO_4$ or $LiBF_4$). All reactions have been performed by using a 1:1 ratio of sulfenyl chloride to olefin[39] and proceeded to give complicated mixtures of products. By use of the procedure of ref 19a, the separation and preparative isolation of products was performed by using preparative TLC on silica gel. The data on the reactions of sulfenyl chlorides with olefins **8–10** are given in Table I,[40] and the structural assignments are discussed below.

Addition to the Triene 8. Reaction of NBSC with triene **8** in AcOH gave four principle products. **11a**, **12a,b**, and **13a** (Chart III). The structure of the unrearranged adduct, chloride **11a**, was established readily by examination of the ^1H NMR spectrum, owing to the presence of characteristic olefinic signals, as well as by comparison with an authentic sample, obtained in a nonpolar medium.[34b] The ^1H NMR spectra of **12a,b** and **13a** do not contain the olefinic protons which is an indication of their rearranged nature. The rearranged product with the "least structural change" has to possess the structure corresponding to the tetracyclo[6.1.1.$0^{2,7}$.$0^{5,9}$] decane skeleton, **15**, owing to the cross-bonding participation of the second double bond[37,41] and subsequent attack at C_6 by the nucleophile. Hence, the structural assignment must include (i) the identification of the skeleton structure as, in particular, of the cross-bonded skeleton of type **15** and (ii) the evaluation of the configuration of the nucleophilic moiety as, for example, for the substituent at C_6 in an exo–endo sense relative to the basal six-membered ring. The compounds with a skeleton of type **15** have been investigated extensively in literature,[32,33,42] but the structures of only three of them have been proven unambiguously by X-ray diffraction data, namely, δ-lactones **7** (X = 2-$NO_2C_6H_4S$)[37a] and **7** (X = Br)[29] and iodoperchlorate **16**.[43]

Although the skeleton of type **15** has been assigned to the majority of the compounds investigated in literature on the basis of **1H** NMR data, a critical examination of the spectra reveals, in fact, the absence of any rigorous criteria for the structural assignments,[45] and to date the best criterion is the "pictoral resemblance" of the signals for the skeletal protons for the compounds with known structure with those of the ones under investigation. As a standard for a skeleton of type **15** we have chosen iodide **16**,[43] for which the ^1H NMR spectrum is presented in Figure 1 (supplementary material) together with the spectra of some of the compounds under investigation. The comparison clearly indicates the resemblance of the signal patterns in **12b** with the ones in the model compound. Analogous comparisons have led to similar conclusions in all of the following cases, as, for example, with the chloride **12a**.

The configurational assignments of the substituents at C_6 for the derivatives of type **15** has been made by using the experimental data for the model compounds **7** (X = 2-$NO_2C_6H_4S$ and X = Br) and **16** where the $H_{6\text{-exo}}$ signals are a doublet of doublets with $J_{H_6\text{-exo}-H_5}$ in the range of 6–8 Hz and $J_{H_{6\text{-exo}}-H_7}$ in the range 0–3 Hz. Inspection of the Dreiding model supports the possibility of a large coupling constant (more than 6 Hz) for the *exo*-H_6 and predicts the appearance of a small coupling constant (0–4 Hz) for the *endo*-H_6. As is seen from Figure 1, the signal for the AcO–C_6–H in **12b** is a doublet with J = 6.0 Hz. In the ^1H NMR spectrum for the hydroxy derivative **12c**, obtained from acetate **12b**, the signal of HO–C_6–H is also a doublet with J = 6.0 Hz. These data both indicate that the coumpounds **12b** and **12c** have the endo configuration of the functional groups at C_6. In contrast, the spectrum of the chloride **12a** contains a doublet for the signal of Cl–C_6–H with J = 3.5 Hz which indicates the exo position for the chlorine atom (see below the data for **12d** and **12e**).

The forth isolated compound, acetate **13a**, has a completely different skeletal pattern in its ^1H NMR spectrum as shown in Figure 2 (supplementary material), especially a characteristic low-field signal for the AcO–C–H proton (δ 5.8) and three upfield multiplets (δ 1.3, 1.7, and 1.9) belonging to the protons of a cyclopropane moiety. The structure of **13a** was unambiguously determined by an X-ray diffraction study[22b] to be dimethyl 5-[(2-nitrophenyl)thio]-10-acetoxytetracyclo[4.4.0.$0^{2,4}$.$0^{3,7}$]dec-8-ene-8,9-dicarboxylate.

Reaction of NBSC with triene **8** under doping-addition conditions in the presence of $LiBF_4$ gave two previously obtained compounds, **12b** and **13a**, and the new fluoride **12f**, the structure of which is consistent with its ^1H and ^{19}F NMR data. Addition of NBSC to **8** in acetonitrile produced mainly the cross-bonded, poorly soluble amide **12g** in a yield of 52% which can be increased up to 71% in the presence of $LiBF_4$.

However the most amazing result which has been observed in this reaction under doping conditions in the presence of $LiClO_4$,[18–26] which also leads to the mixture of the two acetates **12b** and **13a**, is, astonishingly, the formation of a mixture of isomeric perchlorates **12d** and **12e**. These compounds are reasonably stable, at least enough to obtain a satisfactory elemental analysis, but explode at the melting point. The perchlorates are conveniently identified on TLC by an initial heating of the TLC plate to induce a characteristic decay with formation of a black spot. This feature permits one to easily identify the perchlorates obtained (vide infra). The TLC of a mixture of the perchlorates **12d** and **12e** exhibits a single spot. However, the ^1H NMR spectrum of this sample indicates that it is a mixture of two stereoisomers, *exo*-C_6 (δ 5.0, $J_{H_6\text{-endo}-H_7}$ = 2.5 Hz) and *endo*-C_6 (δ 4.75, $J_{H_6\text{-exo}-H_5}$ = 6.0 Hz) in a ratio of 2:1.

The course of the reaction of DNBSC with the triene **8** in AcOH and under doping conditions is analogous, in general, to the previously described reactions with NBSC; the product distributions for these reactions are also summarized in Table I. The structural assignments for

(39) (a) In some cases the total yiels are appreciably less than 100% which is due to the 1:1 ratio of ArSCl and olefin used. Under these conditions a part of the ArSCl is evidently consumed in a reaction with the solvent (see, e.g., ref 39b). Actually this complication could be responsible for the formation of the product with a low R_f value observed in some cases (cf. ref 18). We did not make any attempts to optimize the total yields by variation of ArSCl/olefin ratio. (b) Schmid, G. H.; Csizmadia, V. N. *Int. J. Sulfur Chem.* **1973**, *8*, 433.

(40) In some cases the formation of additional minor products (less than 5%) have been detected by TLC.

(41) Inagaki, S.; Fujimoto, K.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.

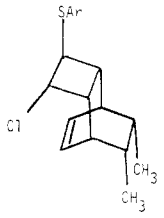
(42) Sasaki, T.; Kanematsu, K.; Kondo, A. *J. Org. Chem.* **1974**, *39*, 2246.

(43) (a) The iodo perchlorate **16** was obtained in a new reaction of perchloration of olefins[44a] by the addition of iodine to diester **8** in the presence of $LiClO_4$ (for X-ray data see ref 43b). (b) Bondar, V. M.; Rau, T. F.; Rau, V. G.; Struchkov, Y. T.; Zefirov, N. S.; Koz'min, A. S.; Zhdankin, V. V.; Kirin, V. N., accepted for publication in *Cryst. Struct. Commun.*

(44) (a) Zefirov, N. S.; Koz'min, A. S.; Zhdankin, V. V.; Kirin, V. N.; Sergeev, B. G. *Zh. Org. Khim.* **1980**, *16*, 1085. (b) Zefirov, N. S.; Zhdankin, V. V.; Nikulin, A. V.; Zyk, N. V.; Koz'min, A. S. *Ibid.* **1981**, *17*, 210.

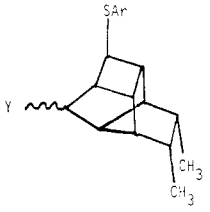
(45) The most serious criterion has been the following:[42] "...the absence of NOE and spin-decoupling between H_x and H_a".

Chart IV



17a, Ar=2-$NO_2C_6H_4$

17b, Ar=2,4-$(NO_2)_2C_6H_3$



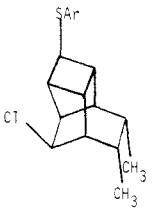
18a, Ar=2-$NO_2C_6H_4$, Y=anti-OAc

18b, Ar=2-$NO_2C_6H_4$, Y=anti-$OClO_3$

18c, Ar=2,4-$(NO_2)_2C_6H_3$, Y=syn-Cl

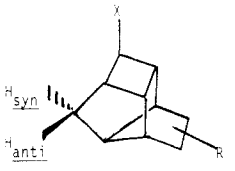
18d, Ar=2,4-$(NO_2)_2C_6H_3$, Y=anti-OAc

18e, Ar=2,4-$(NO_2)_2C_6H_3$, Y=anti-$OClO_3$



19a, Ar=2-$NO_2C_6H_4$

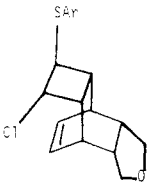
19b, Ar=2,4-$(NO_2)_2C_6H_3$



23

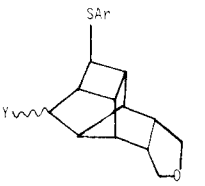
X = SAr

Chart V



24a, Ar=2-$NO_2C_6H_4$

24b, Ar=2,4-$(NO_2)_2C_6H_3$



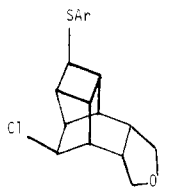
25a, Ar=2-$NO_2C_6H_4$, Y=anti-OAc

25b, Ar=2-$NO_2C_6H_4$, Y=anti-$OClO_3$

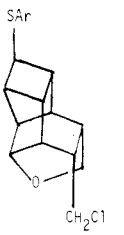
25c, Ar=2,4-$(NO_2)_2C_6H_3$, Y=syn-Cl

25d, Ar=2,4-$(NO_2)_2C_6H_3$, Y=anti-OAc

25e, Ar=2,4-$(NO_2)_2C_6H_3$, Y=anti-$OClO_3$



26, Ar=2-$NO_2C_6H_4$



27a, Ar=2-$NO_2C_6H_4$

27b, Ar=2,4-$(NO_2)_2C_6H_3$

12h–j and **13b** have been made analogously to the NBSC series, and only one point needs a special comment. Addition of DNBSC to the triene **8** in AcOH in presence of a large excess of added $LiClO_4$ gave three principal products. One of them is the acetate **12h**, and the second is a mixture of the perchlorates **12i** and **12j**. The ^1H NMR spectrum of the third compound, **14** exhibited the presence of olefinic protons of a cyclobutene ring. An X-ray diffraction study has shown that **14** is dimethyl 9-*endo*-acetoxy-10-[(2,4-dinitrophenyl)thio]tricyclo[4.3.1.$0^{2,5}$]-deca-3,7-diene-7,8-dicarboxylate.[46] These data suggest that the formation of **14** is due to the unprecedented endo attack on the double bond incorporated in the six-membered ring with a subsequent Wagner–Meerwein rearrangement.

Addition to the Dienes 9 and 10. The reactions of ArSCl with the dienes **9** and **10** proceed in the same manner, and we shall discuss these results together. The experimental data are collected in Table I. First of all, the identification of the skeletal structure for some of the compounds obtained was met with difficulties. In order to unequivocally establish the structure of the rearranged products, X-ray diffraction studies of acetates **18a**[22a] and **25a**,[47] perchlorate **18e**,[48] and chloride **25c**[49] (see Charts IV and V) were performed. These data reveal two points of importance: (i) the compounds investigated have the skeleton of tetracyclo[5.3.0.$0^{2,5}$.$0^{3,8}$]decane (**23**), and hence we revealed a novel type of Wagner–Meerwein rearrangement; (ii) the configuration (see **23**) at C_6 for the chloride vs. that for the acetate is opposite; the chloride **25c** has the syn configuration while acetates **18a** and **25a** have the anti configuration. These X-ray data permitted us to make the ^1H NMR identification of skeleton **23** vs. **15** as well as the configurational assignment for the C_6 center in the series **18** and **25**.

As is shown in Figure 3 (supplementary material), the ^1H NMR spectra of the anti isomers **18a,e** and **25a** contain the singlet signals for the H_6 proton (the examination of Dreiding models suggests a small coupling constant, $J \approx 0$–2 Hz). In the cases for the syn configuration at C_6 (Figure 3, compounds **18c** and **25c**), these signals are a doublet of doublets with $J \approx 8.0$–8.5 and 3.0–3.5 Hz.

However, we wish to emphasize that ^1H NMR criteria for the skeletal assignment is not very rigorous in some cases, and the structural assignments must be taken as probable but not as definitely proven. For example, we have not been able to separate the material obtained in a yield of 25% in the addition of NBSC to **9** in AcOH, and we assumed it to be the 1:1 mixture of chlorides **19a** and **20**. This mixture gave one spot on TLC plates in different systems, but its NMR spectrum contains two different signals for HCCl in the form of a broad singlet at ~4.3 ppm and a doublet at ~4.5 ppm with $J = 2.0$ Hz. The last signal permitted us to assign to one of the components of the mixture the structure of the cross-bonded *exo*-chloride **19a**, while the structure of second compound, **20**, is still undetermined.

We also failed to determine the structure for the com-

(46) (a) A suitable crystal of **14** was obtained by evaporation of ethyl acetate–hexane solution. Crystal data:[46b] $a = 8.53$ (3) Å, $b = 10.129$ (4) Å, $c = 14.155$ (5) Å, $\alpha = 85.29$ (3)°, $\beta = 83.76$ (3)°, $\gamma = 81.44$ (3)°; space group $P\bar{1}$; $Z = 2$; $R_{hkl} = 0.041$. (b) Sedov, B. B.; Rau, V. G.; Struchkov, Y. T.; Zefirov, N. S.; Koz'min, A. S.; Kirin, V. N.; Zhdankin, V. V., accepted for publication in *Cryst. Struct. Commun.*

(47) (a) A suitable crystal of **25a** was obtained by evaporation of hexane solution. Crystal data:[47b] $a = 8.695$ (5) Å, $b = 18.77$ (1) Å, $c = 11.948$ (6) Å, $\beta = 112.59$ (5)°; space group $P2_1/n$; $Z = 4$; $R_{hkl} = 0.060$. (b) Sedov, B. B.; Rau, V. G.; Struchkov, Y. T.; Ilyukhin, V. V.; Belov, N. V., accepted for publication in *Dokl. Akad. Nauk SSSR.*

(48) (a) A suitable crystal of **18e** was obtained from a hexane–ethyl acetate mixture. Crystal data:[48b] $a = 16.75$ (1) Å, $b = 9.069$ (5) Å, $c = 13.339$ (9) Å, $\beta = 106.31$ (5)°; space group $P2_1/c$; $Z = 4$; $R_{hkl} = 0.074$. (b) Yufit, D. S.; Rau, V. G.; Struchkov, Y. T.; Koz'min, A. S.; Kirin, V. N.; Zhdankin, V. V.; Zefirov, N. S., accepted for publication in *Cryst. Struct. Commun.*

(49) (a) A suitable crystal of **25c** was obtained from a methylene chloride solution. Crystal data:[49b] $a = 9.441$ (2) Å, $b = 9.731$ (3) Å, $c = 19.236$ (6) Å, $\beta = 97.71$ (2)°; space group $P2_1/n$; $Z = 4$; $R_{hkl} = 0.047$. (b) Sedov, B. B.; Rau, V. G.; Potekhin, K. A.; Struchkov, Y. T.; Koz'min, A. S.; Kirin, V. N.; Zefirov, N. S., accepted for publication in *Cryst. Struct. Commun.*

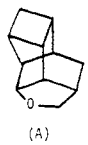
pound **21**, which was obtained by the doping addition of NBSC to diene **9** (Table I). This compound shows the presence of two cyclic unsubstituted double bonds and the ArS moiety in the NMR spectrum. In our preliminary report[22b] we suggested for **21** the structure of 5-hydroxy-4-[(2-nitrophenyl)thio]-9,10-dimethylbicyclo[4.2.2]deca-2,7-diene, but it still remains very speculative. Unfortunately, we have not been successful in obtaining the single crystal of **21** necessary for an X-ray study. In the reaction of DNBSC with **9**, the NMR data permitted us to establish the structures for the chlorides **17b** (for details see ref 34b) and **18c** (Figure 3). However, we have not been successful in separating the mixture of the chlorides obtained in a total yield of 18%. Taking into account the corresponding result for the NBSC addition to **9** and the NMR data of this mixture (the availability of two signals for HCCl at 4.6 and 4.4 ppm), we believe that one of the compounds is the cross-bonded *exo*-chloride **19b**, but the structure of the second compound, **22**, is still in question.

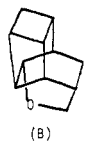
The addition of NBSC to the diene **10** in AcOH proceeds to give 5% of the acetate **25a**[47] and three chlorides (69%). One of them is definitely chloride **24a**.[34b] The structure of the second chloride has been ascribed to **26** due to the pattern for the HCCl signal in the cross-bonded skeleton (doublet at 4.8 ppm, J = 2.0 Hz). The structure of the third minor chloride **27a** (7% yield) was suggested by the similarity of the ^{1}H NMR data with those for compound **27b** (vide infra). The addition of DNBSC to diene **10** in AcOH also gives three chlorides. Unambiguous proof for two of them, **24b** and **25c**, was made on basis of ^{1}H NMR spectra[34b] and X-ray data.[49] However, the structural assignment for the third chloride **27b** is still very speculative, because we could not obtain a single crystal for an X-ray investigation.[50]

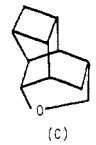
The reactions of dienes **9** and **10** with NBSC and DNBSC in the presence of lithium perchlorate proceeded with the formation of fewer products, all of which were the result of Wagner–Meerwein rearrangements, including the perchlorates **18b,e** and **25b,e** (Table I). The formation of the chlorides **27a** or **27b** under these conditions has not been observed.

In summary, we should like to emphasize that X-ray data for these series were of extraordinary importance and permitted us to determine the structures of the majority of the isolated compounds.

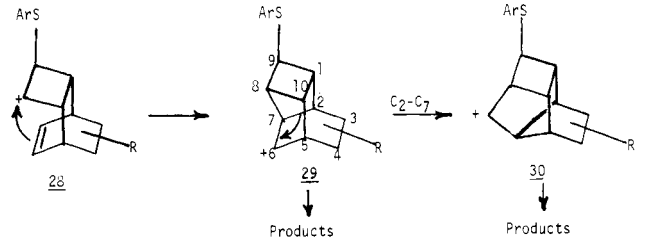
(50) (a) The ^{1}H NMR spectrum of **27b** exhibits the absence of vinyl protons and the presence of complicated overlapping signals in the region of 4.0–1.8 ppm. These patterns are different from the typical NMR patterns of the tetrahydrofuran moiety of all derivatives of **10**, which usually contain the methylene resonance at 3.7 and 3.3 ppm. For further confirmation of the structure we undertook the study of ^{1}H and ^{13}C NMR spectra of this compound, obtained from the specially prepared d_4-labeled (in the tetrahydrofuran moiety) starting material **10**. The ^{1}H NMR spectrum of the resulting compound **27b** was simplified in the low-field region and exhibited resonance of one proton for the substituent at 4.1 ppm in the form of doublet of doublets (J = 2.2 and 7.6 Hz). This data seems to indicate the opening of the original tetrahydrofuran moiety and the occurrence of the pathway which resembles route B of Scheme I. The rupture of tetrahydrofuran ring has been previously observed for the bromination product of diene **10**,[50b] to which the structure with a skeleton of either 11-oxapentacyclo[5.4.1.0^{2,9}.0^{3,6}.0^{4,8}]dodecane (A) or 12-oxapentacyclo[6.4.0.0^{2,5}.0^{4,7}.0^{3,10}]dodecane (B) has been ascribed. Taking into account the analogy with γ-lactone ring closure,[29,37a,41,43b] the most preferential skeleton for **27** seems to be 9-oxapentacyclo[6.4.0.0^{2,5}.0^{3,7}.0^{6,10}]-dodecane (C). (b) Farnum, D. G.; Snyder, J. P. *Tetrahedron Lett.* **1965**, 3861.


(A)


(B)


(C)

Scheme II



Discussion

The most important results of the present study are the following: (1) the reactions investigated are sensitive to the doping effect; (2) novel types of skeletal rearrangement of the Wagner–Meerwein type leading to unusual caged structures have been found; (3) a rare example of rearrangement for ArSCl addition has been found in a moderately polar solvent (CH_3COOH), data which clearly supports the ion-pair mechanism for the addition[8,18,25a] which, in turn, leads to several important mechanistic and stereochemical conclusions; (4) the unique process of covalent bonding of perchlorate anion in the second step of electrophilic addition has been observed. These points are developed below.

(1) Skeletal Rearrangements and the Effect of Doping. As mentioned at the beginning of this paper, reference data indicate that skeletal rearrangements in RSCl addition reactions have been observed only in very rare cases.[3,7,9] Even *tert*-butylethylene,[51] bicyclo[2.1.1]-hex-2-ene,[5b] 10,11-dimethyldibenzobicyclo[2.2.2]octatriene,[52] and benzvalene,[53] all especially liable to undergo skeletal rearrangements, have been shown to form the normal products of trans 1,2-addition. The reactions of RSCl with nonconjugated dienes proceed as the consecutive independent additions to each of the double bonds.[3,7,54]

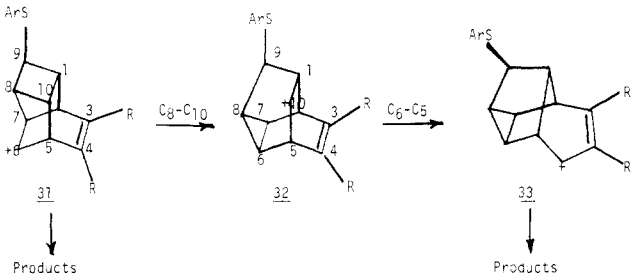
Addition of ArSCl to the polycyclic models **8–10** in a nonpolar solvent (CCl_4) shows the analogous behavior: the exclusive formation of 1,2-addition products have been observed.[34] The features of the reactions in AcOH shall be discussed later. Here we should only like to mention the appearance of a second pathway resulting from the participation of the second double bond and formation of rearranged compounds in AcOH. Thus, the change of the solvent polarity ($CCl_4 \rightarrow$ AcOH) leads to an appreciable change in the product structures.

Even more remarkable changes occur under doping conditions (see Table I). The additions in the presence of $LiClO_4$ do not exhibit the formation of the *trans*-chloro sulfides of types **11**, **17**, and **24** but lead to a miscellanea of new pathways. Most of them yield products either of skeletal rearrangements of different types or of the incorporation of external nucleophiles from the solvent pool. Both of these features are typical ones for carbenium ion like processes. Thus, the addition of lithium perchlorate leads to an increase in the effective electrophilicity of sulfenyl chlorides to such an extent that the total process reveals electrophilic features typical of carbocationic ones.

In this section we will focus the discussion on the rationalizations of the mechanistic pathways to grasp the structural features of the rearranged products using pure

(51) Mueller, W. H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 482. Dean, C. L.; Garratt, D. G.; Tidwell, T. T.; Schmid, G. H. *J. Am. Chem. Soc.* **1974**, *96*, 4958.
(52) Cristol, S. J.; Kochansky, M. C. *J. Org. Chem.* **1975**, *40*, 2171.
(53) Katz, T. J.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1974**, *96*, 1948.
(54) Schmid, G. H.; Yeroushalmi, S.; Garratt, D. G. *J. Org. Chem.* **1980**, *45*, 910.

Scheme III



carbenium ion symbols and stepwise presentations for the sake of simplicity. With the exception of **14** (vide infra), all observed pathways include the exo direction for the initial attack of the electrophile on the cyclobutene double bond. The initial carbenium ion then interacts in a transannular fashion with the proximal double bond of the six-membered ring to create a cationic species of type **29** (Scheme II). This results in the generation of a transient positive charge on these double-bonded carbon atoms by the participation of the second proximal double bond in six-membered ring (**28** → **29**) and the transannular σ-bond formation, affording the cationic species of type **29**. The trapping of the carbenium ion intermediate **29** by different nucleophiles leads to a variety of isolable products, some expected (e.g., **12a,b**) and some surprising (e.g., **12d,e**; vide infra). This mode of transannular rearrangement was commonly observed in reactions of tricyclo[4.2.2.$0^{2,5}$]-deca-3,7-diene derivatives with strong electrophiles.[29,42,55] The preferential cross bonding was elegantly explicated by Fukui and co-workers[41] in terms of three-orbital mixing. Hence, the cross structures of type **29** are the first rearranged intermediates which are produced with the "least structural changes".

However, the cage structure of such compounds as **18** and **25** clearly indicates that the rearrangement process does not cease at the stage of the cationic species of type **29** but proceeds further, producing the products of a novel Wagner–Meerwein rearrangement. Indeed, to rationalize the formation of these compounds, one needs to postulate an unforeseen additional rearrangement process, namely, a 1,2-shift of the C_2–C_7 bond in a species of type **29** to give the new cationic structure of type **30**. The competitive attack on **30** by nucleophiles gives final products such as the chlorides **18c** and **25c** and the acetates **18a,d** and **25a,d** (for discussion of their stereochemistry, vide infra). Thus, the sequence of cross bonding of the double bonds followed by the 1,2-shift of the C_2–C_7 bond affords the novel type of cage compounds of the **18** and **25** series.

In the case of the triene system **8**, the rearrangements observed are even more fascinating. The cross bonding due to the participation of the proximal unsubstituted double bond leads analogously to the species of type **31** (Scheme II), and also gives rise to a number of products of type **12**. However, the mode of the following rearrangement is completely different. Instead of a 1,2-shift of the C_2–C_7 bond, which would be analogous to the above rearrangement (**29** → **30**), one needs to assume the occurrence of two subsequent 1,2-shifts of the C_8–C_{10} and C_5–C_6 bonds, affording the cationic species of type **32** and **33**, respectively. It is surprising that the rearrangement, which includes a transannular bond formation and two 1,2-shifts, leads to the formation of the products **13** which contain a cyclopropane ring. In fact, the loss of a small-membered ring and its replacement with a five- or six-membered one is usually considered to serve as a driving force for many rearrangements because the stability of the new skeleton may be felt in the transition state.

Thus, it is of interest to discuss the reason for the selection between the competitive pathways (a) **29** → **30**, with migration of the C_2–C_7 bond in the reaction of the diene compounds **9** and **10**, and (b) **31** → **32**, with migration of the C_8–C_{10} bond and then the C_5–C_6 bond in the reaction of the triene system **8**. The energy of the transition state for a Wagner–Meerwein rearrangement depends also on the effectiveness of orbital overlap which depends on the initial alignment of relevant groups. To some extent, the development of the p orbital at C_6 in the course of cross bonding, **28** → **29**, can be supported by rear-side attack of migrating the C_2–C_7 bond, **29** → **30**. An examination of stereomodels shows that this migrating bond and the p orbital at C_6 may be nearly in one plane after the small and progressive distortion associated with the "turn away" movement of C_7 (see structure **29**). For the process involving C_8–C_{10} bond migration in **31** → **32**, one has to assume front-side attack on the p orbital at C_6. In this case the carbocationic site and the migrating bond are evidently not in one plane initially. Hence, the first pathway, **28** → **30**, seems to be more favorable, and some other stabilization factors probably operate for the second pathway, **31** → **33**. It is possible that *the participation of the third substituted double bond in aiding the stabilization of the developing cationic center at C_{10} in **32** represents such an additional factor and determines the preference of the second pathway, **31** → **33***. The spatial arrangement of the migrating C_8–C_{10} bond and the participating double bond around C_{10} are advantageous for an interaction of this type. The participation of a proximal double bond in the stabilization of a carbocationic center has been discussed previously.[56] For example, the retention of configuration in the solvolysis of 7-norbornadienyl tosylate has been rationalized in terms of π participation.[56b] In our case, the process of the subsequent (C_6–C_5) bond migration to the cationic center at C_{10}, **32** → **33**, also proceeds with retention of configuration at C_{10}. It seems impossible to accept a concerted mechanism for these two migrations, **31** → **32** and **32** → **33**. However, the hypothesis of double bond participation in migration of the C_8–C_{10} bond and stabilization of the cationic center at C_{10} naturally explains the selection of the C_6–C_5 bond for the second migration as well as the retention of configuration at C_{10}.

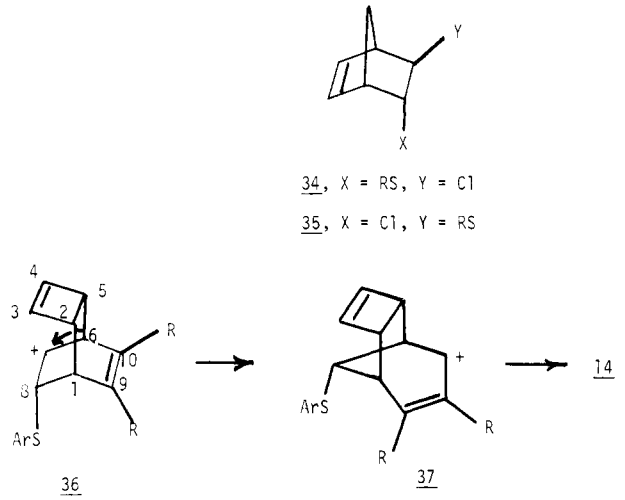
The next unusual type of rearranged structure is represented by compound **14**. First of all, in this case one must accept an initial electrophilic attack on the less strained double bond of the six-membered ring from an endo direction. The occurrence of this competitive pathway is not fully understood. It is worthy to mention that another typical bicyclic diene, norbornadiene, has been observed to give products resulting from primary endo attack by electrophilic agents more often than the corresponding norbornene.[57] For example, the addition of DNBSC to norbornadiene in AcOH proceeds to give two trans 1,2-adducts, **34** and **35** (see Scheme IV), with normal and "inverted" trans configurations, respectively.[26] Hence,

(55) Sasaki, T.; Kanematsu, K.; Kondo, A.; Okada, K. *J. Org. Chem.* **1976**, *41*, 2231. Sasaki, T.; Kanematsu, K.; Kondo, A. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2516.

(56) (a) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; Chapter 3. (b) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183. Winstein, S.; Shatavsky, M. *Ibid.* **1956**, *78*, 592.

(57) Lautenschlaeger, F. *J. Org. Chem.* **1966**, *31*, 1679. Gregocic, A.; Zupan, M. *Tetrahedron* **1977**, *33*, 3243. See also ref 25a and references therein.

Scheme IV



one might suspect that 1,4-arrangement of double bonds in a six-membered ring of a bicyclic (e.g., norbornadiene) or cage system might influence the direction of electrophilic attack. Second, this endo electrophilic attack (**8** → **36**) is followed by the 1,2-migration of the C_5–C_6 bond, affording the cationic species of type **37**. Unexpectedly, the conceivable competitive process of transannular participation by the cyclobutene double bond does not take place. The discussed pathway, with formation of **14**, was observed only on addition of a massive amount of $LiClO_4$, and its influence on the reaction mode is not as yet explicable.

(2) Criteria and Chemical Consequences of the Ion-Pair Mechanism of the ArSCl Addition to Olefins. As was mentioned at the beginning of this paper, the operation of the doping effect suggests the intermediacy of the intermediates **2–4** that are less polar than episulfonium ions **1** in the ArSCl addition under normal conditions. In light of this, it is constructive to analyze the presence data with ArSCl additions in CH_3COOH in order to gain some insight into the best choice of the possible intermediates with different S···Cl bonding.

Let us pose the question: how is it possible to differentiate, in principle, the ion-pair vs. purely ionic mechanism of addition? The structure of the ion pair must include some sort of bonding between the negatively charged ion (*chloride* anion in the present case) and the electrophilic moiety (sulfur atom). Hence, *the experimental criteria of an ion-pair mechanism have to take into account the more manifested participation of the counteranion in the final step of the reaction as compared with the purely ionic mechanism.* First, one has to observe the increased participation of the counteranion in competition with the nucleophilic solvent in the case of an ion-pair mechanism. In other words, this criterion takes into account the different chemoselectivity of ion-pair vs. ion processes. For the ArSCl addition it means increasing the ratio of chlorides to acetates as the S···Cl bonding is increased in the intermediate (**1** → **4**). Second, an ion-pair mechanism is clearly exhibited in the case of rearranged processes (carbocationic-like intermediate) which proceed to give the rearranged chlorides (but not acetates). This criterion resembles the so-called "internal return" process of ion pairs in solvolysis. Third, the ion-pair bonding between chlorine and sulfur may lead to an unusual stereochemical configuration for the products, because the specificity of the ion-pair structure can determine the route of migration of the chloride ion in the final step of addition. For example, the ion-pairing phenomena may lead to a preference for one particular stereochemical pathway and hence to an exclusive preference for one of the epimeric structures.[14]

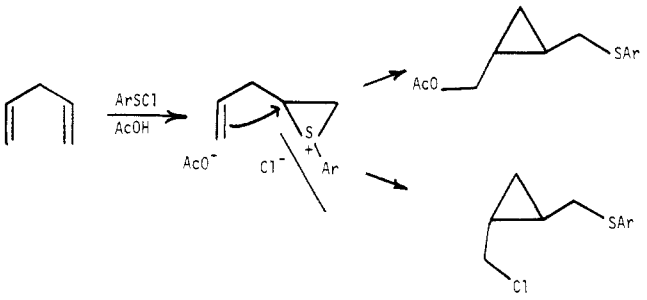
In this section we will discuss the operation of the two first criteria. In our previous approach to this problem,[19a] we used these two criteria to choose between the species **2–4** as possible intermediates. The first criterion, which is directly connected with the chloride/acetate ratio, revealed the involvement of two different types of intermediates: one being a sort of "loose" one (increased content of acetates) and the other being a "tight" one (increased content of chlorides). A "loose" intermediate has been associated with the solvent-separated ion pair **2**; however, two candidates, namely, sulfurane **4** and the tight ion pair **3**, can represent the "tight" intermediate. The second criterion, involving the formation of rearranged chlorides, reveales the involvement of tight ion pairs **3**. Indeed, this process must include the intermediacy of the species which (a) possess a significant positive charge on carbon atoms, at least large enough to lead to a rearranged product, and (b) somehow keep the S···Cl bonding during the whole process leading to the formation of chlorides without the incorporation of external nucleophiles. We have shown that this type of ion-pair intermediate depends on both the structure of the olefin and of the sulfenyl chloride. For example, the addition of DNBSC to dimethoxybenzonorbornadiene in AcOH proceeds via the tight ion pair **3**, whereas the same reaction with norbornene involves the solvent-separated ion pair **2**.[19a]

It is useful to consider the data of Table I for the reactions in AcOH in light of these criteria. The examination of the data of Table I for the reactions of NBSC and DNBSC does not reveal appreciable differences. However, the comparison of the chloride/acetate ratio shows a remarkable dependence on the structure of the olefin. Indeed, the additions of ArSCl in AcOH to the triene **8** proceed to give mainly the acetates (of rearranged structures), while the analogous additions to the dienes **9** and **10** proceed predominantly with the formation of chlorides. In accordance with the first criterion one may conclude that the addition to the dienes **9** and **10** involves a "tighter" intermediate for the product-determining step than for the addition to the triene **8**.

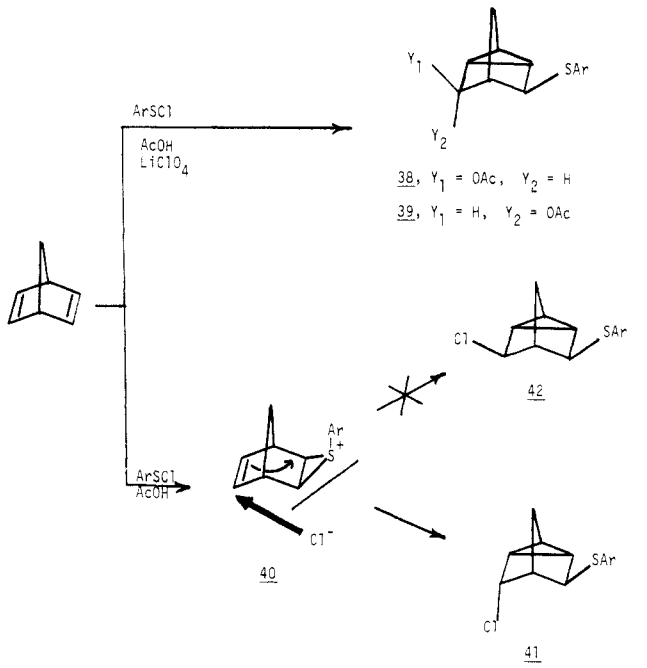
The consideration of the second criterion supports this conclusion. Indeed, the addition to the dienes **9** and **10** proceeds to give appreciable amounts of *rearranged* chlorides in the nucleophilic media which, as stated above, may be regarded as an indication of the involvement of a some sort of "tight" intermediate which bears a positive charge on carbon at least sufficient enough for the participation of the second double bond, but without the full separation of the chloride anion. This conclusion was supported further by using the stereochemical criterion (vide infra). On the other hand, the additions to the triene **8** in AcOH give mainly acetates, which means that these reactions not only involve appreciable development of the positive charge on the carbon atom, inducing the participation of the second double bond, but also must involve a relatively large degree of ionization of the S···Cl bond in a "loose" intermediate. However, the operation of the doping effect suggests that even a larger separation of ions and, hence, the intermediacy of a more electrophilic species, is possible.

To simplify the pictorial representation of the mechanism, we interpret these arguments in terms of the tight ion pair **3** for the addition of ArSCl in AcOH to the dienes **9** and **10** and in terms of the solvent-separated ion pair **2** for the triene **8**.

Scheme V

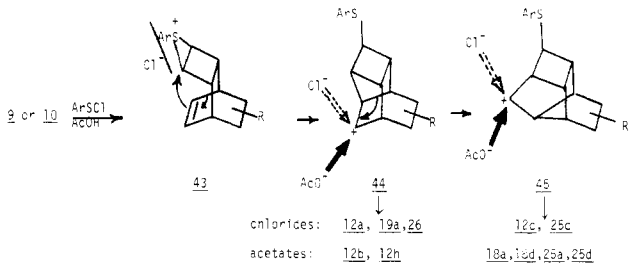


Scheme VI



(3) Stereoselectivity in the Ion-Pair Mechanism for ArSCl Additions. The involvement of ion pairs in the addition process may lead to important stereochemical consequences. Previously we have discussed briefly the concept of stereocontrol by an ion-pair mechanism in an electrophilic addition.[19a,25a,26a] As stated above, the formation of rearranged chlorides in AcOH supports the intermediacy of ion pairs **3**. One only has to assume an internal attack on the positively charged center in the ion pair by its own chloride counteranion to give the resulting rearranged chloride. Hence, the stereochemistry of the resulting chloride may be constrained to the spatial structure of the corresponding ion pair. In some cases this situation may lead to a difference in configuration of the chloride as compared with the products resulting from attack by an external nucleophile, e.g., acetate. This statement is shown schematically in Scheme V by using a model homoconjugated diene system. It is expedient to review the experimental data which can be regarded as being supportive of this concept. We previously have shown that doping addition of NBSC and DNBSC to norbornadiene proceeds with participation of a second double bond to give two isomeric acetates **38** and **39**[26a] (Scheme VI). In accordance with ref 58, the nonstereospecific attack by the nucleophile indicates the involvement of a carbocationic-like intermediate. However, the addition of ArSCl in AcOH together with the 1,2-addition products **34** and **35** proceeds with homoallylic participation to give the single nortricyclenic chloride **41** with an endo configuration for chlorine.[26,59-61] Hence the stereochemical course of the addition is completely different depending upon whether the attack was by an external (**38**, **39**) or internal (**41**, i.e., belonging to the tight ion pair **40**) nucleophile. These data seem to support the general concept because the endo configuration of chlorine may be naturally explained in terms of the ion-pair mechanism **40** → **41**.

Scheme VII



It is also useful to compare the configurations of the rearranged chlorides vs. those of the rearranged acetates. The structures of **18a**, **25a**, and **25c** have been unabiguously determined by X-ray analysis and clearly show the opposite configuration of Cl vs. OAc: the attack by AcO^- proceeds with *inversion* while the attack by Cl^- proceeds with *retention* of configuration at C_7. The observed configurational difference may be explained in an analogous fashion by an ion-pair mechanism, **43** → **44** (Scheme VII), by accepting syn-internal attack on ion **45** by Cl^- and anti-external attack by AcO^- from the solvent pool.

The configurational assignments for the series **12** and **19** have been made only by NMR. These compounds also seem to exhibit the same configurational difference between the chlorides (e.g., **12a**) and the acetates (e.g., **12b**). Again, this difference may be easily rationalized in terms of an ion-pair mechanism, **43** → **44** → **45**. In conclusion, the remarkable difference in configuration for the chlorides vs. the acetates in the series **12**, **18**, and **25** may be regarded as additional experimental verification of the concept of stereochemical control of addition by an ion-pair mechanism.[19a,25a,26a]

(4) Incorporation of External Nucleophiles and Products of Addition. Doping addition of sulfenyl chlorides opens new pathways for the incorporation of external nucleophiles. For example, we described previously the reactions of concerted 1,2-thioacetylation[19,21] and 1,2-thioamidation of olefins[23] in the presence of $LiClO_4$.[63]

(58) Cristol, S. J.; Harrington, J. K.; Singer, M. S. *J. Am. Chem. Soc.* **1966**, *88*, 1529.

(59) (a) We are using exo–endo terminology for the nortricyclene system in accordance with ref 59b with respect to the unsubstituted CH_2 group. (b) Cristol, S. J.; LaLonde, R. T. *J. Am. Chem. Soc.* **1958**, *80*, 4355.

(60) (a) Reactions of norbornadiene with NBSC and DNBSC under doping conditions and in the presence of lithium chloride also gives the other isomeric chloride with exo configuration of chlorine atoms.[60b] (b) Sadovaya, N. K.; Novgorodtseva, L. A., private communication.

(61) We have determined the structure of **39** by X-ray diffraction[26b] because the unambiguous configurational assignment of 3,5-disubstituted nortricyclenes by usual NMR spectroscopy methods is difficult. In fact, the authors of ref 62 ascribed to the nortricyclenic chlorosulfides the exo exo configuration **40** on the basis of NMR data. However, a careful examination of data in ref 62a reveals an inconsistance in the applied criteria for an unambiguous configurational assignment. We are planning to pursue this problem (together with Professor T. C. Morrill).

(62) (a) Garratt, D. G.; Beaulieu, P. L. *J. Org. Chem.* **1979**, *44*, 3555. (b) Beaulieu, P. L.; Kabo, A.; Garratt, D. G. *Can. J. Chem.* **1980**, *58*, 1005, 1014, 1030.

(63) The increased yield of the products of mixed 1,2-addition with incorporation of the solvent in presence of $LiClO_4$ has been observed for bromination[64a] but not for the chlorination[64b] in AcOH. For the effect of perchlorates on the ring-opening of epoxides see ref 65.

(64) (a) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1477. (b) Yates, K.; Leung, H. W. *J. Org. Chem.* **1980**, *45*, 1401.

In good agreement with these data, the additions in the presence of added electrolytes lead to the formation of rearranged acetates due to the participation of an external nucleophile (acetic acid) in the final step of the addition. We even observed the incorporation of an acetonitrile moiety with formation of the amide **12g** in the addition of NBSC to triene 8. Some other unanticipated results of these reactions are discussed below.

First, the attempt to dope the addition reaction of NBSC to triene 8 by $LiBF_4$ led, in part, to a pathway involving the abstraction of fluorine from BF_4^- to give the fluoride **12f**. Such a rather rare pathway has been previously observed in a number of investigations for a variety of carbocationic processes.[17,66] Evidently the rearranged cationic intermediate of type **29** under our doping conditions is "hot" enough to react with a superweak nucleophilic species such as BF_4^- with abstraction of fluorine.

Second, the most remarkable result is formation and isolation of the covalent perchlorates **12d,e,i,j**, **18b,e**, and **25b,e**. The ClO_4^- ion is usually considered to be a superweak nucleophile, and the possible formation of perchlorates in processes of electrophilic addition in presence of other nucleophiles is usually ignored. The addition of $LiClO_4$ to a reaction mixture is a generally accepted tool to increase the ionic power of media without the danger of contamination from additional nucleophilic species.

However, some kinetic data provide an example of carbenium perchlorate ion-pair return to covalent perchlorates.[65,67] Moreover, several organic perchlorates have been obtained via substitution reactions in inert media.[68] These covalent perchlorates are usually extremely unstable and exhibit explosive properties.[68] The sole exceptions are the sulfonylmethyl perchlorates, $RSO_3CH_2OClO_3$, which have been isolated in an analytically pure state[69] (for X-ray data, see ref 69b).

The perchlorates obtained in the present paper are comparatively stable although they also vary in stability and reactivity. The perchlorates of series **12** are more stable than those of series **18** and **25** and can be isolated in a pure form. A slow increase in temperature even permits one to determine melting points (see Experimental Section). The explosion of a sample occurs only during rapid heating. Preliminary work has shown that the resulting perchlorates are sufficiently stable to solvolysis and do not produce the corresponding acetates or chlorides.

The mechanism for the perchlorate formation is not understood in full detail. The stereochemical results, namely, the nonstereospecific addition to 8 and the anti configuration of perchlorate **18e**, seem to indicate that the perchlorate anion is taken from the media but not from the perchlorate ion pair, the formation of which is conceivably due to the exchange of the counterion Cl^- with the ClO_4^- in ion pairs of type **2** or **3**.

In conclusion, we emphasize that the results presented here are the first cases of the participation of the perchlorate anion as a nucleophile in the final step of a mixed electrophilic addition in the presence of other and more reactive nucleophilic species. This finding could be significant in helping one to understand the question of nucleophilicity[70] as well as of some other phenomena where perchlorate participation is important (see, for example, the discussion about the origin of the "special salt effect" in solvolysis[15]). The isolation of the perchlorates has stimulated us to investigate this problem in more detail. We now have elaborated the conditions for preferential formation of perchlorates for a variety of electrophiles, including halogens, sulfenyl chlorides, and nitronium borofluoride, with a variety of olefins.[44] These results permit us to state that the *electrophilic perchloration of olefins (e.g., chloroperchloration, etc.) is a new reaction that is general in scope.*

Experimental Section

General Methods. The melting points were determined with a micro melting point apparatus in open capillary tubes and are uncorrected. Microanalyses were performed in the Laboratory of Microanalyses of the Chemical Department of Moscow State University. The NMR spectra were obtained in the indicated solvents on a varian ST-60 or JEOL XL-100 spectrometers unless otherwise noted. Tetramethylsilane was used as an internal standard, and the chemical shifts are expressed in δ values. The IR spectra were taken with a UR-10 infrared spectrophotometer as Nujol suspensions. Analytical and preparative thin-layer chromatography was carried out by using silica gel 40/100 or 5/40 on 18 × 24 cm TLC plates. The removal of material from the silica gel was accomplished by successive washings with ethyl acetate. The starting olefins were prepared according to ref 32b and 38 and purified by recrystallization.

Reactions of 8 with NBSC. (A) In Acetic Acid. To a solution of 8 (0.98 g) in acetic acid (20 mL) was added NBSC (0.76 g). The solution was stirred for 22 h and then poured into water (50 mL). The mixture was extracted with methylene chloride (4 × 15 mL). The organic layer was washed with a saturated solution sodium bicarbonate (3 × 30 mL) and then with water (2 × 50 mL) and was dried ($MgSO_4$). The solvent was removed by evaporation, and the oily residue was adsorbed on a silica gel column and chromatographed. Elution with methylene chloride give **11a** (0.4 g; R_f 0.22; mp 139–140 °C[34b]), **12a** (0.1 g), **12b** (0.75 g), and **13a** (0.25 g).

For **12a**: yellow oil; R_f 0.11; IR 1725, 1640, 1600, 1570, 1525, 1340 cm^{-1}; NMR (100 MHz, CCl_4) 8.2–7.1 (4 H, m), 4.0 (1 H, d, J = 3.5 Hz), 3.7 (6 H, 2 s), 3.4–2.2 (7 H, m).

Anal. Calcd for $C_{20}H_{18}ClNO_6S$: C, 55.11; H, 4.16; Cl, 8.13; N, 3.21. Found: C, 54.90; H, 4.25; Cl, 7.86; N, 3.87.

For **12b**: mp 153 °C (methanol); R_f 0.05; IR 1740, 1710, 1640, 1600, 1570, 1520, 1340 cm^{-1}; NMR (295 MHz, $CDCl_3$) 8.3–7.3 (4 H, m), 4.9 (1 H, d, J = 6.0 Hz), 3.9 (3 H, s), 3.8 (3 H, s), 3.6 (1 H, dd, J = 5.5, 1.5 Hz), 3.5 (1 H, dd, J = 7.5, 6.0 Hz), 3.4 (1 H, s), 3.2 (1 H, dd, J = 5.5, 2.0 Hz), 2.7 (1 H, dd, J = 5.0, 2.0 Hz), 2.6 (1 H, dt, J = 7.5, 5.0, 5.0 Hz), 2.3 (1 H, dd, J = 5.0, 1.5 Hz), 2.0 (3 H, s).

Anal. Calcd for $C_{22}H_{21}NO_8S$: C, 57.51; H, 4.61; N, 3.05; S, 6.98. Found: C, 57.40; H, 4.57; N, 2.82; S, 7.15.

For **13a**: mp 168–170 °C (methylene chloride–pentane, 1:1); R_f 0.07; IR 1745, 1730, 1720, 1650, 1600, 1570, 1520, 1340 cm^{-1}; NMR (100 MHz, $CDCl_3$) 8.2–7.1 (4 H, m), 5.8 (1 H, m), 3.8 (3 H, s), 3.7 (3 H, s), 3.5 (1 H, d, J = 1.0 Hz), 2.8 (1 H, dd, J = 1.8, 1.3 Hz), 2.7 (1 H, dd, J = 3.5 and 1.6 Hz), 2.1 (1 H, m), 2.0 (3 H, s), 1.9 (1 H, 1:1:2:2:1:1 sextet, J = 5.0, 5.0, 1.6 Hz), 1.7 (1 H, ddd, J = 5.0, 5.0, 1.0 Hz), 1.3 (1 H, 1:1:2:2:1:1 sextet, J. = 5.0, 5.0, 1.4 Hz). For the X-ray data, see ref 22c.

Anal. Calcd for $C_{22}H_{21}NO_8S$: C, 57.51; H, 4.61; N, 3.05; S, 6.98. Found: C, 56.95; H, 4.43; N, 2.97; S, 7.16.

(65) (a) Pocker, Y.; Ronald, B. P. *J. Am. Chem. Soc.* **1980**, *102*, 5311.
(66) Chackelford, S. A. *J. Org. Chem.* **1979**, *44*, 3485. Kanischev, M. I.; Schegolev, A. A.; Smit, W. A.; Caple, R.; Kelner, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 5660. Balenkova, E. S.; Frolov, E. B.; Anfilogova, S. N. *Zh. Org. Khim.* **1978**, *14*, 1109. Anfilogova, S. N.; Folov, E. B.; Lusikov, Y. N.; Balenkova, E. S. *Ibid.* **1979**, *15*, 1432.
(67) Ehret, A.; Winstein, S. *J. Am. Chem. Soc.* **1966**, *88*, 2048.
(68) (a) For brief reviews see: Burton, H.; Praill, P. F. G. *Analyst (London)* **1955**, *80*, 4. Dorofeenko, G. N.; Krivun, S. V.; Dulenko, V. I.; Zhdanov, Y. A. *Russ. Chem. Rev. (Engl. Transl.)* **1965**, *34*, 88. (b) Some alkyl perchlorates have been obtained by the addition of $HClO_4$ (from $LiClO_4$ and concentrated H_2SO_4) to olefins: Hoffman, D. M. *J. Org. Chem.* **1971**, *36*, 1716. (c) Nelsen, S. F.; Calabrese, J. C. *J. Am. Chem. Soc.* **1973**, *95*, 8385.
(69) (a) Bruggink, A.; Zwanenburg, B.; Engberts, J. B. F. N. *Tetrahedron* **1969**, *25*, 5655. Menninga, L.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1976**, *98*, 7652. (b) Engberts, J. B. F. N.; Morssink, H.; Vos, H. *Ibid.* **1978**, *100*, 799.
(70) Hudson, R. F. In "Chemical Reactivity and Reaction Paths"; Klopman, G., Ed.; Wiley: New York, 1973; Chapter 5.

(B) In Acetic Acid and in the Presence of $LiClO_4$. A solution of **8** (0.6 g), NBSC (0.5 g), and lithium perchlorate (0.5 g) in acetic acid (10 mL) was sitrred for 1 h and then poured into water (20 mL). The resulting mixture was extracted with methylene chloride (5 × 10 mL). The organic extract was washed with a solution of sodium bicarbonate followed by water (2 × 20 mL), dried ($MgSO_4$), and stripped of solvent. The oily residue was subjected to column silica gel chromatography (methylene chloride) to give **12b** (0.44 g), **13a** (0.22 g), and **12d + 12e** (0.20 g).

For **12d + 12e**: mp 124 °C dec; R_f 0.26; IR 1730, 1640, 1600, 1570, 1520, 1345 cm^{-1}; NMR (100 MHz, $CDCl_3$) 8.3–7.3 (4 H, m) 5.0 and 4.75 (1 H, 2 d, J = 2.5, 6.0 Hz), 3.9 (3 H, s), 3.8 (3 H, s), 3.5–2.4 (7 H, m).

Anal. Calcd for $C_{20}H_{18}ClNO_{10}S$: C, 48.06; H, 3.63; Cl, 7.09; N, 2.80; S, 6.41. Found: C, 48.00; H, 3.47; Cl, 7.67; N, 3.04; S, 6.13.

(C) In Acetic Acid and in the Presence of $LiBF_4$. A solution of **8** (1.2 g), NBSC (0.9 g), and lithium fluoroborate (1.3 g) in acetic acid (30 mL) was stirred for 5 h. The usual workup furnished an oily residue which was separated by column silica gel chromatography. Elution with methylene chloride gave the first fraction (R_f 0.5) which was subjected to thin-layer chromatography on silica gel by using ethyl acetate–cyclohexane (1:3) and gave **11a** (0.08 g), **12b** (1.2 g), **13a** (0.51 g), and **12f** (0.2 g).

For **12f**: mp 158–160 °C (methylene chloride–pentane, 1:1); R_f 0.11 (ethyl acetate–hexane, 1:3); IR 1730, 1640, 1595, 1580, 1520, 1343 cm^{-1}; NMR (100 MHz, $CDCl_3$) 8.3–7.0 (4 H, m), 5.3 (1 H, m), 3.9 (6 H, 2 s), 3.7–2.1 (7 H, m); ^{19}F NMR (100 MHz, CCl_4, measured from $CFCl_3$) 163.5 (dt, J_{H-F} = 32.5, 12.0, 12.0 Hz).

Anal. Calcd for $C_{20}H_{18}FNO_6S$: C, 57.27; H, 4.33; N, 3.34; S, 7.64. Found: C, 56.80; H, 4.30; N, 3.26; S, 7.81.

(D) In Acetonitrile. A solution of **8** (0.1 g) and NBSC (0.08 g) in acetonitrile (2 mL) was kept at room temperature for 5 days. The precipitate was collected by filtration and washed with water. Crystallization from methylene chloride gave **12g**: 0.1 g; mp 229 °C dec; R_f 0.75 (acetonitrile); IR 3280, 1730, 1660, 1600, 1570, 1520, 1330 cm^{-1}; NMR (60 MHz, $CDCl_3$) 8.3–7.1 (4 H, m), 5.7 (1 H, m, exchangeable by D_2O), 4.2 (1 H, m), 3.8 (3 H, s), 3.7 (3 H, s), 3.5–2.1 (7 H, m), 1.9 (3 H, s).

Anal. Calcd for $C_{22}H_{22}N_2O_7S$: C, 57.63; H, 4.84; N, 6.11; S, 6.99. Found: C, 57.40; H, 4.89; N, 6.00; S, 7.14.

(E) In Acetonitrile and in the Presence of $LiBF_4$. A mixture of **8** (1.0 g), NBSC (0.8 g), lithium fluoroborate (1.6 g), and acetonitrile (10 mL) was stirred for 10 h. The usual workup as described in D gave **12g** (1.3 g).

Reactions of 8 with DNBSC. (A) In Acetic Acid. A solution of **8** (1.0 g) and DNBSC (0.95 g) in acetic acid (20 mL) was stirred for 24 h and then poured into water (50 mL). The mixture was extracted with methylene chloride (5 × 20 mL). The organic layer was washed with a saturated solution of sodium bicarbonate (3 × 50 mL) and then with water (2 × 50 mL). Drying ($MgSO_4$) and removal of solvent gave a yellow oil which was adsorbed on a silica gel column and chromatographed. Elution with chloroform gave **11b** (0.55 g; mp 167 °C; R_f 0.3 ($CHCl_3$)[34b]), **12h** (1.05 g), and **13b** (0.13 g; see next procedure).

For **12h**; mp 172–173 °C (hexane–methylene chloride, 1:1); R_f 0.15 ($CHCl_3$); IR 1745, 1710, 1640, 1600, 1540, 1525, 1345 cm^{-1}; NMR (80 MHz, $CDCl_3$) 9.0–7.2 (3 H, m), 4.8 (1 H, m), 3.8 (6 H, 2 s), 3.7–2.2 (7 H, m), 1.9 (3 H, s).

Anal. Calcd for $C_{22}H_{20}N_2O_{10}S$: C, 52.38; H, 4.00; N, 5.55; S, 6.36. Found: C, 52.04; H, 4.09; N, 5.28; S, 6.34.

(B) In Acetic Acid and in the Presence of 2 Equiv of $LiClO_4$. A solution of **8** (1.0 g), DNBSC (0.95 g), and lithium perchlorate (0.86 g) in acetic acid (20 mL) was stirred for 10 h. The usual workup as described in A gave a yellow oil which was adsorbed on a silica gel column and chromatographed. Elution with methylene chloride gave **12h** (0.96 g), **13b** (0.31 g), and a mixture of **12i** and **12j** (0.4 g).

For **13b**: mp 153–155 °C (ethyl acetate–hexane, 1:2); R_f 0.3 (methylene chloride); IR 1730, 1660, 1600, 1525, 1350 cm^{-1}; NMR (60 MHz, $CDCl_3$) 9.1–7.2 (3 H, m), 5.9 (1 H, m), 3.9 (3 H, s), 3.8 (3 H, s), 3.6 (2 H, m), 2.9 (1 H, m), 2.7 (1 H, m), 2.3 (1 H, m), 2.0 (3 H, s), 2.0–1.4 (3 H, m).

Anal. Calcd for $C_{22}H_{20}N_2O_{10}S$: C, 52.38; H, 4.00; S, 6.36. Found: C, 51.87; H, 4.12; S, 6.80.

For **12i + 12j**: mp 151–153 °C dec; R_f 0.4 (methylene chloride); IR 1730, 1650, 1600, 1530, 1350 cm^{-1}; NMR (80 MHz, $CDCl_3$) 9.1–7.2 (3 H, m), 5.3 and 5.0 (1 H, 2 d, J = 6.0, 2.5 Hz), 3.9 (3 H, s), 3.8 (3 H, s), and 3.8–2.3 (7 H, m).

Anal. Calcd for $C_{20}H_{17}ClN_2O_{12}S$: C, 44.09; H, 3.14; Cl, 6.51; N, 5.14; S, 5.88. Found: C, 44.96; H, 3.54; Cl, 6.38; N, 5.02; S, 5.92.

(C) In Acetic Acid and in the Presence of 10 Equiv of $LiClO_4$. A mixture of **8** (1.0 g), DNBSC (0.95 g), lithium perchlorate (4.3 g), and acetic acid (25 mL) was stirred for 1 h at room temperature. The usual workup as described in A and B gave **12h** (0.74 g), a mixture of **12i** and **12j** (0.6 g), and **14** (0.45 g).

For **14**: mp 157–158 °C (ethyl acetate–ether, 1:1); R_f 0.35 (methylene chloride); IR 1750, 1725, 1650, 1600, 1520, 1345 cm^{-1}; NMR (295 MHz, $CDCl_3$) 9.0–7.6 (3 H, m), 6.2 (2 H, d, J = 2.5 Hz), 5.4 (1 H, d, J = 1.7 Hz), 4.1 (1 H, dd, J = 4.0, 3.5 Hz), 3.72 (3 H, s), 3.69 (3 H, s), 3.3 (1 H, d, J = 3.5 Hz), 3.1 (2 H, m), 3.0 (1 H, d, J = 3.5 Hz), 2.0 (3 H, s). For X-ray data, see ref 46.

Anal. Calcd for $C_{22}H_{20}N_2O_{10}S$: C, 52.38; H, 4.00; N, 5.55. Found: C, 52.30; H, 3.89; N, 5.22.

Reactions of 9 with NBSC. (A) In Acetic Acid. A mixture of **9** (0.32 g) and NBSC (0.38 g) in acetic acid was stirred for 30 min at room temperature and poured into water (50 mL). The mixture was extracted by chloroform (2 × 20 mL). The organic extract was washed with a solution of sodium bicarbonate then with water (2 × 20 mL) and dried with sodium sulfate. The solvent was removed in vacuo, and the yellow residue was adsorbed on a silica gel column and chromatographed. Elution with carbon tetrachloride–ethyl acetate–hexane (2:1:3) gave **17a** (0.3 g; mp 143–144 °C (chloroform–hexane, 1:4); R_f 0.49[34b]), **18a** (0.17 g), and a mixture of **19a** and **20** (0.18 g).

For **18a**: mp 133–134 °C (hexane); R_f 0.27; IR 1730, 1594, 1567, 1520, 1340 cm^{-1}; NMR (100 MHz, CCl_4) 8.3–7.1 (4 H, m), 5.1 (1 H, s), 3.2 (1 H, s), 2.0 (3 H, s), 3.1–1.5 (8 H, m), 1.0 (6 H, d, J = 6.5 Hz). For X-ray data, see ref 22b.

Anal. Calcd for $C_{20}H_{23}NO_4S$: C, 64.32; H, 6.21; N, 3.75; S, 8.59. Found: C, 64.19; H, 6.18; N, 3.42; S, 8.80.

For **19a + 20**: yellow oil; R_f 0.38; NMR (CCl_4, 60 MHz) 8.3–7.0 (4 H, m), 4.5 and 4.3 (1 H, d, J = 2.0 Hz, and br s), 3.3–1.7 (15 H, m).

(B) In Acetic Acid and in the Presence of $LiClO_4$. A mixture of **9** (0.7 g), NBSC (0.76 g), lithium perchlorate (2.2 g), and acetic acid (10 mL) was stirred for 20 min at room temperature and then was treated as previously described in A. Preparative thin-layer chromatography on silica gel with ethyl acetate–ether (1:3) gave **18a** (0.7 g), **18b** (0.6 g), and **21** (0.2 g).

For **18b**: mp 80–84 °C dec; R_f 0.8; NMR (60 MHz, $CDCl_3$) 8.3–7.2 (4 H, m), 5.3 (1 H, s), 3.2–0.8 (15 H, m).

For **21**: mp 112–114 °C (carbon tetrachloride–hexane, 1:2); R_f 0.1; IR 3400, 1595, 1570, 1520, 1340 cm^{-1}; NMR (100 MHz, $CDCl_3$) 8.3–7.2 (4 H, m), 6.3 (1 H, d, J = 9.2 Hz), 6.0 (1 H, d, J = 9.5 Hz), 5.8 (2 H, s), 4.6 (1 H, s), 3.5 (1 H, M), 3.0 (1 H, d, J = 10 Hz), 2.3–1.6 (3 H, m), 1.7 (1 H, s), 1.0 (3 H, d, J = 7.1 Hz), 0.9 (3 H, d, J = 6.8 Hz).

Effecting this procedure at 55 °C gave **18a** (0.34 g) and **21** (0.29 g).

Reactions of 9 with DNBSC. (A) In Acetic Acid. A solution of **9** (0.48 g) and DNBSC (0.7 g) in acetic acid (8 mL) was stirred for 30 min at room temperature. The resulting mixture was poured into water (50 mL) and then was extracted with chloroform (2 × 25 mL). The organic extract was washed with a solution of sodium bicarbonate (30 mL) followed by water (2 × 50 mL) and stripped of solvent. The oily residue was subjected to column silica gel chromatography (chloroform–hexane, 2:1) to give **17b** (0.31 g; mp 149–151 °C (chloroform–hexane, 1:4); R_f 0.45[34b]), **18c** (0.18 g), **18d** (0.38 g), and **19b + 22** (0.22 g).

For **18c**: mp 164–166 °C (chloroform–hexne, 1:2); R_f 0.4; IR 1600, 1520, 1344 cm^{-1}; NMR (60 MHz, $CDCl_3$) 9.3–7.3 (3 H, m), 4.7 (1 H, dd, J = 8.5, 3.5 Hz), 3.9 (1 H, s), 3.2–1.6 (8 H, m), 0.9 (6 H, 2 s).

Anal. Calcd for $C_{18}H_{19}ClN_2O_4S$: C, 54.75; H, 4.85. Found: C, 54.25; H, 4.94.

For **18d**: mp 189–190 °C (chloroform–hexane, 1:4); R_f 0.15; IR 1735, 1600, 1522, 1345 cm^{-1}; NMR (60 MHz, $CDCl_3$) 9.3–7.3 (3 H, m), 5.1 (1 H, s), 3.2 (1 H, s), 2.0 (3 H, s), 3.1–1.7 (8 H, m), 0.9 (6 H, 2 s).

Anal. Calcd for $C_{20}H_{22}N_2O_6S$: C, 57.40; H, 5.30; N, 6.69; S, 7.66. Found: C, 57.93; H, 5.42; N, 6.09; S, 7.40.

For **19b + 22**: mp 150–153 °C (chloroform–hexane, 1:4); R_f 0.33 (chloroform–hexane, 2:1); IR 1600, 1520, 1343 cm^{-1}; NMR (60 MHz, $CDCl_3$) 9.3–7.3 (3 H, m), 4.6 and 4.4 (1 H, d with J = 2.5 Hz, and a broad signal), 3.5–1.7 (15 H, m).

Anal. Calcd for $C_{18}H_{19}ClN_2O_4S$: N, 7.9; S, 8.12. Found: N, 6.98; S, 8.02.

(B) In Acetic Acid and in the Presence of $LiClO_4$. A mixture of **9** (0.32 g), DNBSC (0.47 g), Lithium perchlorate (1.07 g), and acetic acid (5 mL) was stirred for 20 min. The usual workup as described in A gave **18d** (0.34 g) and **18e** (0.13 g).

For **18e**: mp 110 °C dec; R_f 0.33; IR 1600, 1520, 1340 cm^{-1}; NMR (60 MHz, $CDCl_3$) 9.3–7.2 (3 H, m), 5.4 (1 H, s), 3.3 (1 H, s), 3.2–1.5 (8 H, m), 1.0 (6 H, 2 s). For X-ray data, see ref 48.

Reactions of 10 with NBSC. (A) In Acetic Acid. A solution of **10** (0.96 g) and NBSC (1.05 g) in acetic acid (12 mL) was stirred for 3 h at room temperature, poured into water (100 mL) and extracted with methylene chloride (3 × 30 mL). The organic layer was washed with water (3 × 30 mL) and dried with sodium sulfate. The solvent was removed by distillation, and the yellow oil was subjected to silica gel chromatography (methylene chloride) to give **24a** (0.7 g; mp 166 °C (carbon tetrachloride); R_f 0.3[34b]), **25a** (0.13 g), **26** (0.54 g), and **27a** (0.14 g).

For **26**: mp 157–158 °C (ethyl acetate–hexane, 1:1); R_f 0.5; IR 1600, 1570, 1510, 1340 cm^{-1}; NMR (60 MHz, $CDCl_3$) 8.3–7.0 (4 H, m), 4.8 (1 H, d, J = 2.0 Hz), 4.0–1.6 (13 H, m).

Anal. Calcd for $C_{18}H_{18}ClNO_3S$: C, 59.42; H, 4.99; Cl, 9.74. Found: C, 58.97; H, 4.83; Cl, 9.28.

For **25a**: mp 174–176 °C (carbon tetrachloride–hexane, 1:1); R_f 0.2; IR 1730, 1600, 1570, 1530, 1320 cm^{-1}; NMR (100 MHz, $CDCl_3$) 8.3–7.2 (4 H, m), 5.1 (1 H, s), 3.7 (4 H, m), 3.2 (1 H, s), 3.1–1.9 (8 H, m), 2.0 (3 H, s). For X-ray data, see ref 47.

Anal. Calcd for $C_{20}H_{21}NO_5S$: C, 62.00; H, 5.46; N, 3.62; S, 8.28. Found: C, 62.20; H, 5.49; N, 3.81; S, 8.31.

For **27a**: mp 157–158 °C (ethyl acetate–hexane, 1:1); IR 1600, 1520, 1345 cm^{-1}; NMR (60 MHz, $CDCl_3$) 8.3–7.2 (4 H, m), 4.8 (2 H, br s), 4.2–18 (12 H, m), 3.3 (1 H, s).

Anal. Calcd for $C_{18}H_{18}ClNO_3S$: C, 59.42; H, 4.99; Cl, 9.74. Found: C, 58.89; H, 4.85; Cl, 9.28.

(B) In Acetic Acid and in the Presence of $LiClO_4$. A mixture of **10** (1.1 g), NBSC (1.2 g), lithium perchlorate (2.8 g), and acetic acid (20 mL) was stirred for 3 h. The usual workup as described in A gave **25a** (0.82 g) and **25b** (1.4 g).

For **25b**: mp 80 °C dec; R_f 0.8; IR 1600, 1570, 1520, 1340 cm^{-1}; NMR (60 MHz, $CDCl_3$) 8.4–7.0 (4 H, m), 4.7 (1 H, m), 4.0–3.5 (5 H, m), 3.3–1.8 (8 H, m).

Anal. Calcd for $C_{18}H_{18}ClNO_7S$: C, 50.53; H, 4.24; N, 3.27; Cl, 8.29. Found: C, 51.48; H, 4.52; N, 3.54; Cl, 8.53; S, 8.49.

Repeating this procedure at 55 °C gave **25a** (0.71 g) and **25b** (1.3 g).

Reactions of 10 with DNBSC. (A) In Acetic Acid. A solution of **10** (1.1 g) and DNBSC (1.5 g) in acetic acid (14 mL) was kept at room temperature for 4 h. The yellow precipitate was filtered, washed with a mixture of carbon tetrachloride–chloroform (1:1) and then chromatographed by preparative TLC on silica gel with 1:2 ethyl acetate–hexane mixture as the eluant. This procedure gave **24b** (0.41 g; mp 183 °C (acetonitrile); R_f 0.3[34b]), **25c** (0.34 g), **25d** (0.21 g), and **27b** (0.88 g).

For **25c**: mp 194–196 °C (hexane–ether, 3:1); R_f 0.4; IR 1595, 1520, 1344 cm^{-1}; NMR (60 MHz, $CDCl_3$) 9.3–7.3 (3 H, m), 4.7 (1 H, dd, J = 8.0, 3.0 Hz), 3.9 (1 H, s), 3.8–2.0 (12 H, m). For X-ray data, see ref 49.

Anal. Calcd for $C_{18}H_{17}ClN_2O_5S$: C, 52.88; H, 4.19; Cl, 8.67; Found: C, 52.95; H, 4.15; Cl, 8.16.

For **25d**: mp 219–221 °C (ethyl acetate–acetonitrile, 1:1); R_f 0.2; IR 1730, 1600, 1540, 1350 cm^{-1}; NMR (295 MHz, $CDCl_3$) 9.3–7.3 (3 H, m), 5.0 (1 H, s), 3.6 (4 H, m), 3.2 (1 H, s), 3.0 (1 H, s), 2.4–1.8 (6 H, m), 2.0 (3 H, s).

Anal. Calcd for $C_{20}H_{20}N_2O_7S$: C, 55.55; H, 4.66; N, 6.48; S, 7.41. Found: C, 55.57; H, 4.69; N, 6.16; S, 7.51.

For **27b**: mp 199 °C (acetonitrile); R_f 0.25; IR 1600, 1540, 1350 cm^{-1}; NMR (60 MHz, Me_2SO-d_6) 9.0–7.4 (3 H, m), 4.0–1.8 (12 H, m), 3.5 (1 H, s).

Anal. Calcd for $C_{18}H_{17}ClN_2O_5S$: C, 52.88; H, 4.19; Cl, 8.67. Found: C, 52.84; H, 4.43; Cl, 8.39.

(B) In Acetic Acid and in the Presence of $LiClO_4$. A mixture of **10** (0.38 g), DNBSC (0.51 g), lithium perchlorate (0.48 g), and acetic acid was stirred for 6 h and poured into water. The mixture was extracted by methylene chloride (2 × 25 mL). The organic layer was washed with a saturated solution of sodium bicarbonate (2 × 50 mL) and then with water (2 × 100 mL). Drying and removal of the solvent in vacuo gave a yellow oil which was chromatographed by preparative TLC on silica gel (12:1 methylene chloride–ethyl acetate) to give **25d** (0.15 g) and **25e** (0.55 g).

For **25e**: mp 115 °C dec (explosive); R_f 0.7; IR 1600, 1520, 1340 cm^{-1}; NMR (60 MHz, $CDCl_3$) 9.0–7.4 (3 H, m), 5.5 (1 H, s), 4.4–1.8 (13 H, m).

Repeating this procedure at 55 °C gave **25c** (0.37 g) and **25d** (0.18 g).

6-*endo*-Hydroxy-9-[(2-nitrophenyl)thio]-3,4-bis(methoxycarbonyl)tetracyclo[6.1.1.$0^{2,7}$.$0^{5,10}$]dec-3-ene (12c) was prepared by refluxing **12b** with oleum in methanol for 2 h: mp 151–152 °C (methanol); R_f 0.05 (silica gel, methylene chloride); IR 3470, 1738, 1712, 1594, 1645 cm^{-1}; NMR (100 MHz, $CDCl_3$) 8.3–7.2 (4 H, m), 4.1 (1 H, d), 3.9 (3 H, s), 3.8 (3 H, s), 3.3 (1 H, d), 3.5–2.3 (7 H, 4 groups of m).

Anal. Calcd for $C_{20}H_{19}NO_7S$: C, 57.55;, H, 4.59; N, 3.36. Found: C, 57.45; H, 4.89; N, 3.41.

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Registry No. **8**, 25157-95-3; **9**, 5773-43-3; **10**, 5773-44-4; **11a**, 79618-68-1; **11b**, 75681-97-9; **12a**, 79702-84-4; **12b**, 79646-91-6; **12c**, 79618-69-2; **12d**, 79646-92-7; **12e**, 79646-93-8; **12f**, 79618-70-5; **12g**, 79618-71-6; **12h**, 79618-72-7; **12i**, 79618-73-8; **12j**, 79646-94-9; **13a**, 79646-95-0; **13b**, 79618-74-9; **14**, 79646-96-1; **16**, 79618-75-0; **17a**, 72034-83-4; **17b**, 75681-91-3; **18a**, 72034-85-6; **18b**, 79618-76-1; **18c**, 79618-77-2; **18d**, 79618-78-3; **18e**, 79618-79-4; **19a**, 79631-83-7; **19b**, 79631-84-8; **24a**, 75681-93-5; **24b**, 75681-90-2; **25a**, 77034-66-3; **25b**, 79618-80-7; **25c**, 76204-00-7; **25d**, 79618-81-8; **25e**, 79618-82-9; **26**, 79618-83-0; **27a**, 79618-84-1; **27b**, 79618-85-2; NBSC, 7669-54-7; DNBSC, 528-76-7.

Supplementary Material Available: Anisotropic temperature parameters and atomic coordinates for compounds **18e** and **25a** (Tables II–VII) and ^1H NMR data for **12b,c**, **13a,b**, **16**, **18a,c,e**, and **25a** (Figures 1–3) (7 pages). For data on **14** and **25c**, see ref 71. Ordering information is given on any current masthead page.

(71) Struchkov, Y. T.; et al. *Cryst. Struct. Commun.* **1980**, *9*, 1039, 1043.