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NEW METHOD FOR INCREASING OF EFFECTIVE ELECTROPHILICITY OF WEAK ELECTROPHILES IN ADDITION REACTIONS. REARRANGEMENTS AND CIS-ADDITION IN REACTIONS OF SULPHENYL CHLORIDES WITH NORBORNENE AND DIMETHOXYBENZONORBORNADIENE

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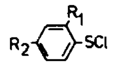
Abstract—The addition of RSCl to norbornene and dimethoxybenzonorbornadiene can proceed with Wagner-Meerwein rearrangement. These addition reactions can also undergo a "doping-effect" which increases the effective electrophilicity of sulfenyl chlorides. Addition of ArSCl to dimethoxybenzonorbornadiene can proceed partially with formation of cis-adduct (**13a**) and of inverted trans-adduct (**12b**). Evidence for the ion-pair mechanism and important mechanistic and stereochemical consequences are discussed.

Recent investigations of the addition reactions of sulphenyl chlorides to olefins have shown, in contrast with general belief (see, for example Refs. 1 and 2), that episulphonium ions are certainly not the intermediates in these reactions in common solvents,[3–6] and that ion pairs are involved in these addition processes.[3–8] We have developed a method for increasing the effective electrophilicity (for definition see Ref. 5) of sulphenyl chlorides, which, in turn, has important synthetic consequences, since a spectrum of new compounds including rearranged structures became available.[3–9] Thus, the most peculiar features of Ad$_E$ RSCl reactions under non-polar conditions are the following:[3,4] (a) these reactions usually proceed without skeletal rearrangements and (b) these addition reactions occur with high trans-stereospecificity (*vide infra*). The application of either "doping" (addition in presence of $LiClO_4$[5,7–9]) or use of a solvent with high ionizing power (e.g. HCOOH[6]) can change the nature of addition products and lead to the rearranged structures. However, contrary to the other Ad$_E$ reactions examples of rearrangements as well as the cases of cis- or non-stereospecific addition in the reactions of sulphenyl chlorides with olefins under usual conditions[10] are extremely rare. Hence, the investigation of these outstanding cases is a matter of interest and importance.

In this paper we describe the addition of arenesulphenyl chlorides **1a–1c** to the norbornene **2**, and to dimethoxybenzonorbornadiene **3** showing that these reactions can occur (i) with Wagner-Meerwein rearrangement and (ii) with the formation of the cis-addition product.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a $R_1 = R_2 = NO_2$
b $R_1 = NO_2$ $R_2 = H$
c $R_1 = H$ $R_2 = Cl$


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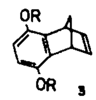
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a $R = CH_3$
b $R = CD_3$

RESULTS

As was observed earlier, the addition of **1a**,[11a] **1b**,[11b] and **1c** to norbornene produces trans-adducts without Wagner-Meerwein rearrangement. Later it was shown[5,6b] that the addition of **1a** to **2** can give five principal products **4a–8a**, their ratio being dependent on conditions. However further studies revealed that the separation method used in Ref. 5 was unsatisfactory for the determination of correct data of product ratio.[12] It was found that preparative tlc on silica gel (*vide infra*) is more reliable and this method was used for all reactions.[6,7,9] The ratio of products provided by this method have been in a good agreement with ^{1}H NMR determination of the product composition in the crude reaction mixture.[*] It is noteworthy that the ratio of products also depends on the initial concentrations of reagents; hence all reactions have been carried out under standard concentration of 1:1 ratio of sulphenyl chloride to alkene. The data on the reactions of **1a–c** with norbornene, **2**, are given in Table 1.

In the preliminary communication [9a] we described the formation of two chlorides **10a** and **11a** by the addition of **1a** to **3** in CCl_4 and CH_3COOH. More thorough investigation with the use of aforementioned method of separation demonstrated that actually the reaction mixture consists of four principal products, **10a**, **11a**, **13a** and **14a**, depending on conditions. The addition of **1b** to **3**

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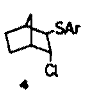
[*] The minor products (<5% of the total) were determined by preparative isolation by tcl; their yields were sometimes not reproducible.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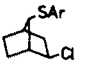
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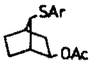
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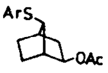
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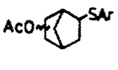
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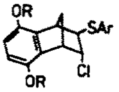
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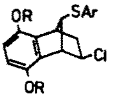
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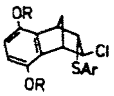
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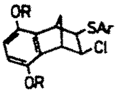
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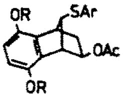
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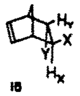
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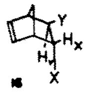
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also gives the four products, **10b**, **11b**, **12b** and **14b**. In a view of overlap of some ^{1}H NMR signals we carried out the reactions of **1a** and **1b** with deuterated olefin, **3b**, and performed the isolation of the products. The ratios of products determined by preparative isolation have been in satisfactory agreement with those determined by ^{1}H NMR. The preparative yields of the products in the addition reactions of **1a** and **1b** to olefins **3** are shown in Table 2.

It may be seen from Tables 1 and 2 that, in some cases, the total yields are appreciably less than 100%. However we have to emphasize that even experiments with relatively low total yields did not show the presence of substantial quantities (>3–5%) the products, different

Table 1. Preparative yields of the products in the addition reactions to the norbornene in CH_3COOH

RSCl	t(C°)	$LiClO_4$/ArSCl	Yields (%)					
			4	5	6	7	7+8	8
1a	20	-	12	40	2	25	35	10
1a	60	-	10	40	5	24	38	14
1a	20	2:1	-	16	2	50^a	75	25^a
1a	60	2:1	-	23	2	30^a	48	18^a
1b^b	20	-	32^a	40^a	5		10	
1b^b	20	2:1	8^a	13^a	8	37^a	60	23^a
1c	20	-	60	-	5		7	
1c	20	2:1	18	-	5	42	72	30

[a] Yield has been determined by NMR only. [b] The acetate 9 (6–10%) has been also isolated.

Table 2. Preparative yields of the products in the addition reactions to olefins 3^a

RSCl	Solv.	t(C°)	$LiClO_4$/ArSCl	Yields (%)				
				10	11	12	13	14
1a	CCl_4	b.p.	-	33	15	-	17	-
1a	AcOH	20	-	5	36	-	trace	9
1a	AcOH	60	-	5	35	-	trace	10
1a	AcOH	20	2:1	trace	26	-	-	47
1b	CCl_4	b.p.	-	56	24	5	-	-
1b	AcOH	20	-	-	92	-	-	5
1b	AcOH	20	2:1	-	44	-	-	50

[a] Both 3a and 3b gave the same products distribution.

from the ones listed in Tables 1 and 2. The decrease in the total yields observed in some cases has been due to the used 1:1 ratio of ArSCl and olefin.[b]

Several comments should be made on the details of structure determinations and analysis of ^{1}H NMR data. The structures of **4a**–**8a** have been proven previously.[5] The configuration of *anti*-acetate **8a** have been unambigously determined by X-ray analysis.[9d] The structures of all the other compounds obtained in this work have been deduced from analysis of ^{1}H NMR spectra. The spectra of norbornenes and norbornanes have been extensively studied[5,6a,14] and this information has been of assistance in interpretation. The gross features of ^{1}H NMR spectra of adducts of benzo-series, **10**–**14**, are shown in Table 3.

Let us consider the key points of the structural assignments. The unrearranged 2,3-disubstituted compounds (e.g. **4**, **10**, **12** and **13**) can be identified by their vicinal J_{23} coupling constant: 3–4 Hz for trans-J_{23} and 7–9 Hz for cis-J_{23}. The 2-exo and 3-exo protons can be assigned by their coupling constant with the bridgehead protons (3–4 Hz). The rearranged structures of norbornane series can be specified by (i) the width of H_2 peak (>10 Hz, $J^{cis}_{23} + J^{trans}_{23}$) and (ii) the sharp singlet of H_7 in the range of 3.1–3.4 ppm. The rearranged structures of type **11** and **14** can be recognized by the signal of 3-CH_2-group which falls in the range of 1.6–2.6 ppm. This multiplet can be interpreted as the AB-part of ABX system with low fields components of this AB pattern (H_A-exo) being further split by coupling with H_4 (exo-H_A is a doublet of triplets, endo-H_B is a doublet of doublets). At the same time, the 7-CH_2 group of unrearranged products of type **10** and **12** appears as a simple AB pattern in the range of 2.0–2.5 ppm.

The peculiar problem of the choice between the trans-structures **10b** and **12b** can be solved using regularities of chemical shifts. The configurational change H_{endo}–C–$X_{exo} \rightarrow H_{exo}$–C–$X_{endo}$ leads to the 0.5–0.8 ppm upfield shift of this signal in ^{1}H NMR spectrum.[14] Hence, we can formulate the general rule of configurational assignment allowing one to make a choice between the structures of type **15** vs **16**: if the X is a sufficiently more electronegative group than Y, then $\delta_{H_X - H_Y}$ sharply increases in going from **15** to **16** and vice versa. For example, the compound **15** (X=Cl, Y = 2,4$(NO_2)_2C_6H_3S$) has δ_{H_X} = 4.1 ppm, δ_{H_Y} = 3.81 ppm and $\Delta\delta$ = 0.29 ppm (in DMSO) compared with δ_{H_X} = 4.34 ppm, δ_{H_Y} = 3.17 ppm and $\Delta\delta$ = 1.17 ppm (in DMSO) for the compound **16** (X=Cl, Y = 2,4-$(NO_2)_2C_6H_3S$).[15]

The choice between syn and anti rearranged isomers has been made using the empirical ^{1}H NMR criterion; the anti-isomer is characterized by low-field shift of H_7 as compared with syn-isomer and vice versa.[6a,9d] In some cases we could not separate the acetates **7** and **8** and have evaluated the isomer ratio by ^{1}H NMR. Only a single acetate **14** has been isolated in addition to olefin **3** and syn-configuration is assigned to it in consonance with mechanistic consideration of Wagner–Meerwein rearrangement.

Finally, the addition of **1b** to **2** has been found to yield also a small quantity (6–10%) of the acetate **9**. ^{1}H NMR spectra of **9** exhibit peaks at 1.83 (s, CH_3COO), 3.0 (S–C–H, m) and 4.53 ppm (O–C–H, m), and coupling between two later peaks is absent. Taking into account literature data[14b] we assume the probable structure **9** for this acetate without additional proof.

DISCUSSION

Before proceeding further, let us briefly consider the general outline of the mechanism of RSCl additions.

Table 3. ^{1}H NMR data of the compounds of benzo series (100 MHz, $CDCl_3$)

Compound	Chemical shifts, δ					Coupling constants (Hz) (±0.3 Hz)		
	H_2	H_3	H_1, H_4	H_7^{anti}	H_7^{syn}	J_{23}	J_{77}	others
10a	4.3(t)	3.14(q)	3.9(m) 3.6(s)	2.0(d)	2.1(d)	3.5	10	J_{12}=3.5 J_{37a} = 2
10b	4.3_6 (t)	3.1_6 (m)	3.96(m) 3.7(s)	2.1 (broad s.)		3.5		J_{12} = 3.7
11a	3.8–3.65 (+H_4)	2.5(exo) 2.07(endo)	3.84(s) 3.8–3.65 (+H_2)	3.60(s)	–	3.7(exo) 7.6(endo)		J_{43exo}=3.7 J_{33} = 13.9
11b	3.8–3.6 (+H_4)	2.56(exo) 2.06(endo)	3.82(s) 3.8–3.6 (+H_2)	3.57(s)	–	3.8(exo) 8.0(endo)		J_{43exo}=3.8 J_{33}=13
13a	4.35 (dd)	3.55 (dd)	3.85(q) 3.68(q)	2.0(m)	2.4_5(dt)	8.0	10	J_{37a} = 1.7 J_{27a} = 1.7
12b	3.95(q)	3.6–3.8 (overlap.m)		2.0(m)	2.33(dt)	4.0	11.2	J_{27a} = 2.2
14a	4.63(q)	1.7–2.4(m) (+CH_3)	3.87(s) 3.6–3.8(m)[a]		–	3.2(exo) 6.8(endo)		
14b	4.60(q)	1.6–2.5(m) (+CH_3)	3.8(s) 3.5–3.7(m)					

[a] not resolved at 300 MHz

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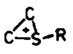
[b] Under the condition used a part of ArSCl is evidently consumed due to the reaction with solvent (see, e.g.[13]). Actually this complication could be responsible for the formation of the untractable product with very low R_f value observed in some cases.

Traditionally these reactions have been described as the two step process involving the intermediacy of episulfonium ions, **17**.[1,2] In contrast, recent investigations presented the experimental evidence for the involvement of less polar intermediates than ions **17**. The solvent-separated ion pairs **18**, tight ion pairs **19**, and covalent sulphurane **20**, could be regarded as such intermediates.[3]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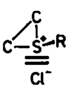
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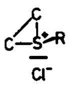
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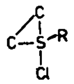
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This conclusion was derived from the following arguments. First, the observed chemical behavior of episulphonium ions has been in striking contrast with the regularities of sulphenyl chloride additions.[3] Secondly, the "doping addition" effect, namely, an escalation of effective electrophilicity due to the addition of a strong electrolyte, constitutes the conclusive and unambiguous evidence of the intermediacy of ion pairs in these addition reactions.[4-9] Indeed, one may pose a question: is it possible to increase the effective electrophilicity of a sulphenyl halide by variation of the conditions? If one accepts the intermediacy of ions **17**, the answer has to be negative because the ions **17** are already the most electrophilic species. We have shown that the answer is definitely positive and the aforementioned "doping-addition" strategem may be used as the test of the ion-pairs mechanism.[3-5] In turn, these investigations pose the following problems: (a) mechanistic distinction of the addition reactions proceeding via different intermediates and (b) elaboration of experimental criteria which identify the particular intermediate.

The most important results of the presented study are the following: (1) Every reaction investigated shows the "doping-addition" effect.[5,7-9] (2) Rare example of the nonsteoeospecific addition of **1a** to olefins **3** with partial formation of the product of cis-addition (**13a**) has been found. (3) Rare examples of skeletal (Wagner–Meerwien) rearrangement have been found in moderately polar (CH_3COOH) and even in non-polar (CCl_4) solvents. (4) The experimental data clearly indicate the involvement of different intermediates in the reaction; that leads to the important mechanistic and stereochemical conclusions.

Ion-pairs mechanism and realization of "doping-addition" effect. As can be seen from Table 1 the addition of **1c** to **2** in AcOH gave mainly chlorides (**4**+**6**, 65%) in spite of the nucleophilic nature of the solvent. This fact demonstrates the absence of complete dissociation of the S–Cl bond and of separation of the counter ions in the course of the addition (*vide infra*). At the same time, the addition of **1a** to **2** in AcOH (Table 1) gave appreciable amounts of acetates. These results show that the intermediate in the addition of **1a** to **2** in AcOH is more polar than the one in the addition of **1c**.

This conclusion can be supported by the kinetic data.[17] The addition of **1c** has been found to proceed slower in AcOH than in $CHCl_2CHCl_2$, which suggests a decrease in polarity of reactants in attaining the transition state. By contrast the addition of **1a** show the opposite solvent effect (AcOH vs CCl_4) and proceeds with an increase in polarity in the transition state which is aided by a more polar medium.

Thus, the chlorides:acetates ratio may be regarded as a criterion of S...Cl bonding in intermediates. In fact, this criterion permits to reveal the involvement of two different type of intermediates: some sort of "loose" (reaction of **1a**+**2**) and "tight" (reaction of **1c**+**2**) ones. Although one can discuss the results in these terms not being definite in their actual determination, this terminology certainly suffers from the lack of structural representation. It is useful to make the correlation between these notions and intermediate species **18**–**20**. A "loose" intermediate can be associated with solvent-separated ion pair, **18**. However, the "tight" intermediate can be associated with both the tight ion pair, **19**, and sulfurane, **20**.[c]

Thus, we suggest *the ratio chlorides : acetates as a diagnostic tool for distinction between the species* **18** *and* **19**+**20**.[18] First case is realized in addition of **1a** to **2**, and the second one in addition of **1c** to **2**.

This mechanistic conclusion can also explain the variation of products distribution in "doping addition" condition. As can be seen from Tables 1 and 2, the course of sulphenyl halide addition can be substantially changed by the addition of $LiClO_4$. That leads to (i) increased content of rearranged products and (ii) incorporation of the solvent (CH_3COOH) in a final step of the addition to give the corresponding acetates. The presence of $LiClO_4$ maximizes the effective electrophilicity of the sulphenyl halide due to (a) the shift of intermediate structure toward a more polar one (e.g. **19**→**18**) and/or (b) the formation of new ion pairs with ClO_4^- counter ion via the anion exchange in solvent separated ion pairs.[3-5,8] Both these mechanisms can operate in the addition of **1c** to give a qualitative change of ratio of products, while the change in the addition of **1a** must be rather quantitative in nature. In fact, the comparison of the data of Table 1 for **1a**, **1b** and **1c** show that the increase of electronegativity of R in the sulphenyl halide RSCl smooths the influence of the added salt. Hence, the doping effect is strongly pronounced for **1c** and only moderate for **1a** in a good accordance with aforementioned mechanistic conclusion.

Skeletal rearrangements in the addition of sulphenyl chlorides to olefins. As mentioned earlier, the skeletal rearrangements have been observed in extremely rare cases.[3,4,19] Even tert-butylethylene[1] and benzvalene[20] (especially liable to undergo rearrangements) have been shown to yield unrearranged 1,2-adducts.

The essential result of this paper is the demonstration of the unusual ease of the skeletal rearrangement in addition reaction of sulphenyl chlorides in solvent of moderate polarity (AcOH) and even in non-polar one (CCl_4). The formation of chloride **11** in CCl_4 evidences the enhanced liability of **3** to react with skeletal rearrangement.

The data of Table 1 show that the addition of **1a** and **1b** proceeds partially with rearrangement which includes the participation of the solvent (AcOH) in the final step of addition with the formation of rearranged acetates **7**+**8**. In contrast, the rearrangements in the additions to

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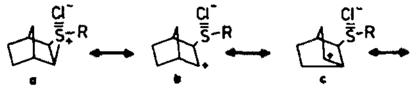
[c] Although the sulphurane **20** has been considered as plausible intermediate[3-6] its intermediacy has not been proven. Recent *ab initio* calculation[16a] showed, that the charge separation, S^+–Cl^-, in these covalent species is rather large, since the chlorine atom has assumed 75% of the full negative charge. Thus, the strict distinction between sulphurane **20** and tight ion pair **19**, may be questionable. Trying to escape the pure semantic extention of the mechanistic problem we shall prefer to use mainly the notion of tight ion pairs; in these terms the sulphurane would be regarded as an ion pair which is "more intimate than intimate".[16b]

olefin 3 proceed in AcOH to give mainly the rearranged chloride 11, but not the acetate 14.

At this point we would like to draw attention to these processes as being characterized by two features: (1) the presence of relatively large positive charge on carbon atom of the intermediate as judged by the formation of rearranged product and (2) the absence of complete dissociation of S–Cl bond as judged by the formation of rearranged chlorides but not acetates. The example of such a process is the formation of 11 in AcOH. We suggest that these features of the process may be regarded as especially clear-cut evidence of the involvement of the tight ion pair intermediate (19). The formation of rearranged chloride 11 both in CCl_4 and AcOH demonstrates ionization but not dissociation of S–Cl bond in intermediate. Hence, we assume that addition of 1a and 1b to 3 proceed via tight ion pair 19 in contrast with the norbornene case. Schematically the structure of intermediates for the addition to 2 and 3 may be represented by formulas 21 and 22 correspondingly. The norbornadiene system in 3 is very sensitive to the cationic charge development and the rearrangement can occur even in tight ion pair intermediate. In contrast, due to a less liability of norbornane skeleton to rearrange (as compare with dimethoxybenzonorbornane one), the appreciable participation of the ionic structures (21b + 21c) can be achieved only under a large degree of ionization of S–Cl bond and of separation of ions as it occurs in solvent-separated ion pair. Hence, the principal rearranged products are the acetates 7 + 8.



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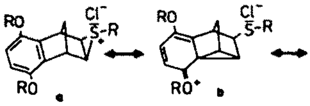

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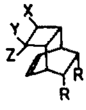
Cis-addition of a sulphenyl chloride to olefins. The well-documented trans-stereospecificity of sulphenyl chloride addition reactions[1,4,21] does not depend on the solvent or the olefin structures, in striking contrast to the variability of the steric course for the majority of Ad$_E$ processes.[22] To the best of our knowledge, only four examples of cis or nonstereospecific addition of a sulphenyl chloride are documented in literature: (a) addition of PhSCl to the cyclobutene double bond of tricyclo[4, 2, 2, $0^{2,5}$]deca-3,7-diene derivatives with the formation of the adduct of type 23 (X=SPh, Y=Cl, Z=H),[23] (b) reaction of 1a with norbornadiene in AcOH with the formation of cis-monoadduct,[24] (c) addition of ArSCl to vinyl ethers,[2a] and (d) the addition of ArSCl to cis and trans anetholes.[2b] First two cases represent the cis-addition to the homoconjugated diene systems and last two cases to the olefins which capable to resonance stabilization of carbenium ion centre.

The reinvestigation of the addition of ArSCl to the derivatives of tricyclo[4, 2, 2, $0^{2,5}$]deca-3,7-diene system (case a) showed the formation exclusively trans-compounds of type 23 (X=SAr, Y=H, Z=Cl) whose structures have been determined by X-ray diffraction.[25] Secondly, reinvestigation of the addition of 1a to norbornadiene showed that cis-adduct was not formed in this reaction. In fact, this process occurs to give the mixture of two isomeric trans-compounds 15 and 16 (X=Cl, Y=$SC_6H_3(NO_2)_2$) together with tricyclene 24.[15] Thus, there are no proved examples of cis-addition of RSCl to the diene systems.



23

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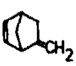

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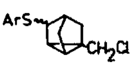

26

In general, the addition to olefins which can form resonance-stabilized cations is expected to be often nonstereospecific due to stabilization of open-ion like vs bridged-ion like intermediates.[1] This situation may be realized for the addition to the anetholes (case d[2b]) as well as to vinyl ethers (case c[2a]). However, the abnormal steric course of an addition reaction may be caused sometimes by thermodynamic control which can be especially important for the β-chloroether product formed in the addition of a sulphenyl chloride to vinyl ethers. The stabilization of the cis-adduct might be due to the conformational factors (for example, due to the gauche[26,27] or anomeric effects[26,28]). For instance, addition to the dihydropyrane occurs with trans stereochemistry at low temperatures; however, a trans-cis-rearrangement occurs at higher temperature.[29] Hence, the data of Ref. 2a have to be considered with caution since the authors have definitely proved the thermodynamic control of the reaction course at elevated temperatures, but have not strictly excluded the possibility of partial equilibration of products at low temperatures. The addition to the anetholes seems to be the single reliable example of a non-stereospecific addition of an arenesulphenyl chloride to an alkene.

Thus, this paper reports the first nonstereospecific addition of a sulphenyl chloride to the strained double bond of a norbornene moiety. Although different explanation of cis-addition in the course of Ad$_E$2 processes has been proposed in literature,[1,30] we believe that the unusual stereochemical result has to be ascribed to the participation of the π-framework with the inclusion of resonance structures of type 22b (*vide supra*). Hence, the nucleophile attack proceeds partially from the opposite side to the new bond to give 13. In summary, we conclude that the formation of cis-adduct 13 is due to the involvement of resonance structure 22b.

Steoeochemical sequence of the concept of ion-pair intermediate in Ad$_E$ reactions of a sulphenyl chloride. As stated above, the concept of the involvement of a tight ion pair 19 can be supported by the formation of rearranged chlorides in AcOH. For that process one has to assume the intramolecular attack of positive charged centre of tight ion pair by its own chlorine atom to produce the resulting chloride. In turn, that leads to the stereochemical sequence of interest; intramolecular transfer of chlorine anion in a final step of addition must involve a particular spatial arrangement. For instance, it has been mentioned that one of the products of the addition of 1a to norbornadiene in AcOH is nortricyclene 24.[15] Now we may predict that it would to have the di-endo-configuration of the substituents. Analogously, the addition of 1a to methylenenorbornene, 25, in AcOH proceeds to give the chloride 26;[31] we may predict the endo-configuration of RS-group in 26. It would be highly desirable to prove these predictions experimentally.[32]

Experimental studies of the consequences of these points are in progress.

EXPERIMENTAL

The deuterated olefin **3b** was prepared according to Ref. 33 and purified by steam distillation. Preparative thin layer chromatography was carried out using silica gel 40/100 or 5/40 μ on the plates 18 × 24 cm. The ^{1}H NMR spectra were obtained in $CHCl_3$ (δ, ppm). Because the yields of the products are listed in Tables 1 and 2 we shall describe below only typical procedures focusing attention on the isolation and characterisation of new compounds obtained. All m.ps are uncorrected. Satisfactory analytical data were obtained for **4c**, **5b**, **6b**, **6c**, **7b** + **8b**, **7c** + **8c**, **10a**, **10b**, **11a**, **11b**, **13a**, **14a** and **14b** (±0.3% for C and H; ±0.4% for Cl and ±0.6% for S).

Addition to norbornene

(a) A soln of **1a** (1g) in AcOH (25 ml) was added to a stirred soln of **2** (0.3 g) in AcoH (10 ml). The mixture was stirred for 2h (20°), then poured in 100 ml water and extracted with $CHCl_3$. The extracts were washed with water, dried over $MgSO_4$, the solvent was removed and residue (1.45 g) was chromatographed twice (hexane: ether = 1:1, SiO_2, 40/100 μ) to give: 0.1 g (12%) of **4a**, 0.3 g (40%) of **5a** and 0.33 g (35%) of mixture **7a** + **8a** together with 2% of **6a**. The latter mixture was chromatographed further (hexane : ethyl acetate = 3 : 1) to give 0.07 g (10%) of **8a** and 0.19 g (25%) of **7a**. The m.p., ^{1}H NMR data and R_f values are in coincidence with given in Ref. 5.

(b) Anhydrous $LiClO_4$(0.4 g) and **2** (0.2 g) were dissolved in 9 ml of AcOH and then 0.4 g of **1b** was added. The mixture was stirred 2h (20°) and analogous work up and chromatography (hexane : ether = 1 : 1, SiO_2 40/100 μ) gave: (i) 0.12 g of mixture of **4b** and **5b** (1:1.5); (ii) 0.05 g (8%) of **6b**, m.p. 136–137° (from petrol ether), ^{1}H NMR spectrum: 3.3 (s, 1H, H–C–S), 3.9 (m, 1H, H–C–Cl); (iii) 0.38 g (60%) of mixture of **7b** + **8b** (2:1), ^{1}H NMR spectrum: 3.3 (s, 1H, H–C–S), 3.6 (s, 1H, H–C–S) 4.62 (q, 2H, H–C–O) and (iv) 0.04 g (6%) of **9b**, m.p. 138.5–139° (from CCl_4), ^{1}H NMR spectrum: 3.0 (m, 1H, H–C–S), 4.53 (m, 1H, H–C–O).

The mixture of **4b** + **5b** was separated by repeated chromatography (hexane : ether = 1 : 1, SiO_2 5/40 μ) to give pure (i) **4b**, m.p. 108°, (from petrol ether), ^{1}H NMR: 3.05 (m, 1H, H–C–S), 3.93 (m, 1H, H–C–Cl). Lit.[11b] m.p. 108.5–109°; (ii) **5b**, m.p. 86–86.5° (from petrol), ^{1}H NMR spectrum: 3.13 (s, 1H, H–C–S).

(c) A soln of **1c** (0.9 g) in AcOH (3 ml) was added to a stirred soln of **2** (0.5 g) and $LiClO_4$ (1 g) in AcOH (10 ml). The mixture was stirred for 0.5 h (20°) and analogous work up and chromatography (hexane : ether : benzene = 3 : 1 : 1, SiO_2 40/100 μ) gave: (i) 0.25 g (18%) of **4c**, R_f = 0.8, distilled at 1 mm Hg (bath temperature 160°), n_D^{20} 1.600, ^{1}H NMR spectrum: 2.94 (t, 1H, H–C–S), 3.88 (t, 1H, H–C–Cl); (ii) 0.06 g (5%) of **6c**, R_f = 0.7, m.p. 80–80.5° (from hexane), ^{1}H NMR: 3.2 (s, 1H, H–C–S), 3.85 (m, 1H, H–C–Cl); (iii) 1.06 g (72%) of mixture of **7c** + **8c** (R_f = 0.5). The later mixture was separated by repeated chromatography to give pure: (i) **7c**, liquid, ^{1}H NMR: 3.1 (s, 1H, H–C–S), 4.66 (q, 1H, H–C–O); (ii) **8c**, liquid, ^{1}H NMR: 3.5 (s, 1H, H–C–S), 4.7 (q, 1H, H–C–O).

Rearranged chloride **6a**. Anhydrous LiCl (1 g) was dissolved in 10 ml anhydrous HCOOH and 0.25 g of **2** and then 0.6 g of **1a** were added. The mixture was stirred for 15 min, poured in water, extracted with $CHCl_3$. The extracts were dried over $MgSO_4$, the solvent was removed and the residue was chromatographed (hexane : ethyl acetate = 3 : 1, SiO_2 5/40 μ) to give: (i) 0.3 g (40%) of **6a**, m.p. 177–178°; (ii) 0.09 g (10%) of mixture of syn and anti 2 - formyloxy - 7 - arylthionorbornanes;[6b] (iii) 0.09 g of mixture of **4a** + **5a**. If the isolation of **6a** was made by recrystallization (twice from CCl_4) the yield of **6a** was of 24% (m.p. 177–178°).

Addition to olefins 3

(a) A soln of **3** (0.56 g) and **1a** (0.66 g) in CCl_4 (50 ml) was refluxed for 2 h. The solvent was removed and the residue was chromatographed (hexane : ethyl acetate = 3 : 1, SiO_2 5/40 μ) to give: (i) 0.4 g (33%) of **10a**, m.p. 185–186° (from EtOH–AcOEt), R_f = 0.73. Lit.[9a] m.p. 177°; (ii) 0.21 g (17%) of **13a**, m.p. 199–200° (from EtOH–AcOEt), R_f = 0.53; (iii) 0.18 g (15%) of **11a**, m.p. 188–189° (from EtOH–AcOEt), R_f = 0.45. Lit.[9a] m.p. 184°.

(b) 0.66 g of **1a** was added to a stirred soln of **3** (0.56 g) and $LiClO_4$ (0.62 g) in AcOH (12 ml). The mixture was stirred for 0.5 h (20°). The usual work up and chromatography ($CHCl_3$, SiO_2 5/40 μ) gave: (i) 0.32 g (26%) of **11a**, m.p. 188–189°, R_f = 0.5; (ii) 0.6 g (47%) of **14a**, m.p. 167–168° (from EtOH–AcOEt), R_f = 0.23.

(c) A soln of **3** (0.66 g) and **1b** (0.6 g) in CCl_4 (50 ml) was refluxed for 2 h. The usual work up and chromatography (hexane : ethyl acetate = 3 : 1, SiO_2 5/40 μ) gave: (i) 0.05 g (5%) of **12b**, m.p. 139.5–140° (from EtOH–AcOEt); (ii) 0.7 g (56%) of **10b**, m.p. 187–187.5° (from EtOH–AcOEt); (iii) 0.3 g (24%) of **11b**, m.p. 134–134.5° (from EtOH–AcOEt).

(d) 0.4 g of **1b** was added to a stirred soln of **3** (0.44 g) and $LiClO_4$ (0.62 g) in AcOH (10 ml). The mixture was stirred for 1 h (20°). The usual work up and chromatography ($CHCl_3$, SiO_2 5/40 μ) gave: (i) 0.37 g (44%) of **11b**, m.p. 133–134°; (ii) 0.45 g (50%) of **14b**, m.p. 163–163.5° (from EtOH–AcOEt).

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