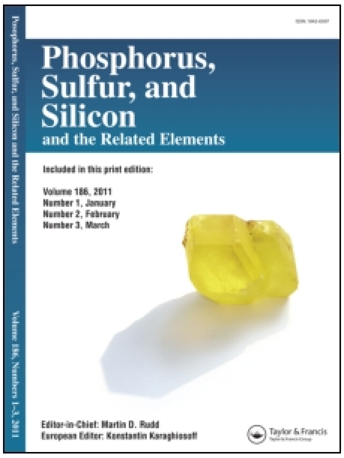

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1,2-ARYL MIGRATION AND EXPERIMENTAL EVIDENCE FOR A TWO-STEP MECHANISM IN THE ELECTROPHILIC ADDITION OF BENZENESULFENYL CHLORIDE TO OLEFINIC SYSTEMS

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1,2-ARYL MIGRATION AND EXPERIMENTAL EVIDENCE FOR A TWO-STEP MECHANISM IN THE ELECTROPHILIC ADDITION OF BENZENESULFENYL CHLORIDE TO OLEFINIC SYSTEMS

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ABSTRACT

Reactions of 2-methyl-3-arylbut-1-en-3-ols (VIII) with benzenesulfenyl chloride were found to give both normal adducts (IX and X) and 1,2-rearrangement products (ketones XI). Yields of XI depend on the electron-releasing effect of the substituents in the benzene ring of VIII. Fairly good correlation of the rate constants with σ° are found, resulting in a ρ_{σ° equal to -0.83. Tetraethylammonium and especially lithium perchlorate addition were found to lead to a sharp increase in the quantity of the rearrangement products (XI). Solvolysis of the adducts IX and X produced enhanced yields of XI as compared with the addition reactions. These facts are clearly consistent with (i) the occurrence of a 1,2-aryl migration in the fast non-limiting step and (ii) suggest a two-step mechanism involving an intermediate with a low degree of positive charge development at the carbon atoms in the rate-determining step.

Since the fundamental work of Kharasch and his co-workers[1,2] in the 1950's, the addition reaction of sulfenyl halides to olefins has found wide synthetic utility.[3,4] Usually this reaction is treated as an electrophilic addition to double bond of an Ad_E 2 type.[5]

This type of an electrophilic addition can be represented by the general Scheme 1.

The addition of the reagents containing a bivalent sulfur atom as an electrophilic center, proceeds in the most cases *via* route C, and skeletal rearrangements are extremely rare.[2,3,5–10] These data suggest that the carbon atoms of an intermediate such as VI or VII bear relatively small positive charges.* This charge resides essentially on sulfur. Therefore, it may be concluded that sulfenyl halides might be considered as "weak electrophiles" as, for example, mercuric salts and nitrosyl chloride (*cf.* refs. 5, 14–19 for discussions of this problem). The addition of the latter electrophiles is accompanied by rearrangements only in rare cases.[20,21]

Recently, it has been reported that 2-methyl-3-arylbut-1-ene-3-ols (VIII) reacted with "strong electrophiles" both *via* route C producing normal addition adducts and *via* route E with 1,2-aryl migration and formation of ketones.[22] Thus, the alkenols VIII have been found to be quite suitable model compounds for the investigation of electrophilic additions.

In this paper we describe a study of the mechanism of the addition of sulfenyl halides using the alkenols VIII as model substrates. We hoped (i) to observe the 1,2-rearrangement in sulfenyl halide addition and (ii) to determine at what step this rearrangement occurs.

Results

The reactions of alkenols VIII with benzenesulfenyl chloride (BSC) were carried out in acetic acid, in CCl_4,

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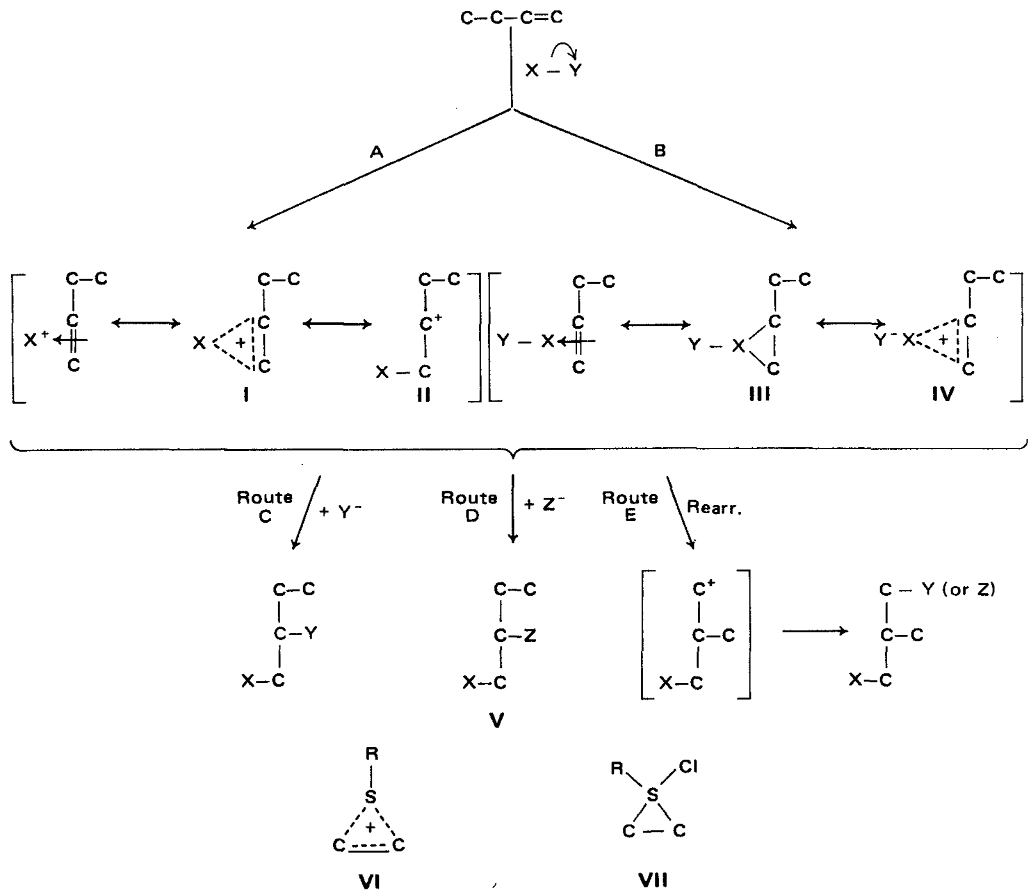
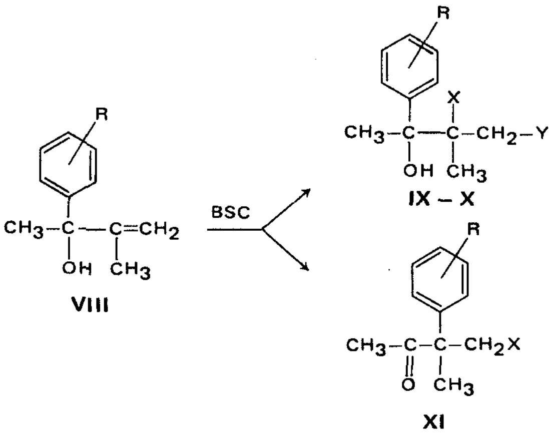
* *This conclusion is also supported by the low sensitivity to the structural features in olefins. For example, the relative rate of chlorination in non-polar media increases 4.3 × 10^5 times in going from 1-butene to tetramethylethylene. On the other hand, the rate of methanesulfenyl chloride addition increases only 12.9 times.*[11,12] *The secondary deuterium isotope effect for the sulfenyl halides additions also suggests significantly more bridging and charge dispersal.*[13]

SCHEME 1



in a mixture of the above solvents (1:3) and in acetic acid in the presence of sodium acetate or perchlorate salts. Yields of rearrangement products (ketones XI) are shown in Table 1.



IX X = Cl, Y = SPh.
X X = SPh, Y = Cl.
XI X = SPh

R = p–CH_3O (a)
p–CH_3 (b)
m–CH_3 (c)
H (d)
p–Cl (e)
m–Cl (f).

The dependence of the yield of ketones XId and XIe on the quantity of the added perchlorate salts is shown in Table 2. Formation of adducts IX and X is apparently an exclusive process in CCl_4. Nmr spectra indicated that mixtures of IX and X (approximately 5:4) were formed. The region from $\delta 2.7$ to 3.7, containing five signals, was of particular interest. These absorptions are made up of a singlet (2H, $-CH_2S-$) at $\delta 3.3$ and a quartet (AB system, J_{AB} = 14 Hz, diastereotopic protons of $-CH_2Cl$). Nmr data are given in Table 3.

The kinetics of the addition reactions have been studied at 25° ± 0.1°, C_0 = 0.01 m/l in 1:3 AcOH–CCl_4. The addition rates are very convenient for measurement under these conditions. The disappearance of BSC was measured and satisfactory second order rate constants were found which are in good agreement with literature data.[23] The rate constants, obtained by the integral method of calculation are listed in Table 1. These data fit the Taft equation[24] excellently, as is shown in Fig. 1. The line has a slope (ρ_{σ°) of –0.83 (r = 0.986, s = 0.04).

We have also studied the solvolysis of the IX and X adduct mixtures in both aqueous acetic acid and aqueous ethanol. Yields of ketones XI are shown in Table 1.

TABLE 1

Kinetics of the Reaction of VIII with BSC and Yields of Ketones XI

Substituent R in benzene ring	Yields of ketones XI (%): Reaction of VIII with BSC, 25°C	75°C	$\frac{[BSC]}{[Et_4NClO_4]} = 7$, 25°	CCl_4-CH_3COOH (3:1), 25° C	Acetolysis of IX and X (0.2 mol/l) CH_3COOH), 75° C	Solvolysis of IX and X: In EtOH-H_2O[a] 25° C	In CH_3COOH-H_2O (9:1) 45°-50° C	K_{av} l/mol . sec CH_3COOH-CCl_4 (1:3), 25° ± 0.2° C_0 = 0.01 mol/l
$p-OCH_3$	80	60		48				0.26 ± 0.02
$p-CH_3$	55	60		25	80	78	42	0.32 ± 0.02
$m-CH_3$						47		0.24 ± 0.01
H	30	30	70	3	68	61	40	0.19 ± 0.01
$p-Cl$	trace	3-5	47	trace	35	35	53	0.13 ± 0.01
$m-Cl$				0		25		0.10 ± 0.01

[a] Run in the presence of 2,4-dinitrophenylhydrazine.

Discussion

Table 1 data show that introduction of the electron-donating substituents into benzene ring of VIII leads to an increase in the 1,2-aryl migration proportion and *vice versa*. This is in accord with the treatment of the 1,2-shift observed as a nucleophilic migration to the positively charged center.

The outstanding features of the reaction investigated are: (i) the correlation of the inductive σ^0 constants and (ii) the low sensitivity of the reaction rate to the substituent effects (low ρ_{σ^0} value).* For example, the ρ_{σ^+} values have been found to be −2.25 ($r = 0.990, s = 0.125$) and −2.75 ($r = 0.990$, $s = 0.161$) for the reactions of alkenols VIII with *t*-butylhypochlorite and *N*-bromosuccinimide (NBS), respectively.[22] We must emphasize, that the log K deviations from good second order for VIIIa and VIIIb, in spite of the large yields of rearrangement products, have not been observed.

All these data suggest that (i) the reaction proceeds *via* an intermediate with a low development of positive charges on carbon atoms in the rate limiting step; (ii) there is no aryl participation in the addition step, which points out the two-step mechanism of the rearrangement; and (iii) an intermediate in the solvolyses should have a more polar structure than the one in an addition reaction. Thus, the addition of BSC to alkenols VIII occurs as a two step process and the

TABLE 2

Influence of the Addition of Perchlorate Salts[a] on the Yields of Rearrangement Products

Addition of $(Et_4)_4NClO_4$ to reaction mixture of VIIId and BSC ($C^0_{VIIId} = C^0_{BSC} = 7 \times 10^{-2}$ mol/l)				
$\frac{C_{BSC}}{C_{Et_4NClO_4}}$		3.5×10^3	3.5×10^2	7.0
Yield of XId, %		36	48	70
Addition of Et_4NClO_4 to reaction mixture of VIIIe and BSC ($C^0_{VIII} = C^0_{BSC} = 7 \times 10^{-2}$ mol/l)				
$\frac{C_{BSC}}{C_{Et_4NClO_4}}$	7×10^3	1.75×10^3	1.75×10^2	7.0
Yield of XIe, %	10	20	37	47
Addition of $LiClO_4$ to reaction mixture of VIIIe and BSC ($C^0_{VIII} = C^0_{BSC} = 3.5 \times 10^{-2}$ mol/l)				
$\frac{C_{BSC}}{C_{LiClO_4}}$	70	35	7	3.5
Yield of XIe, %	19	34	46	51

[a] In the reaction of BSC with VIIIe the yield of XIe was not more than 10% when Bu_4NClO_4 was added.

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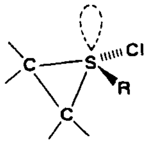
* *The ρ value of −2.35 for the 2,4-dinitrobenzenesulfenyl chloride addition to styrenes has been determined.*[23a] *Values for some electrophilic additions are listed in ref. 23c.*

1,2-aryl migration occurs in the second fast step.† This migration may be considered as an intramolecular alkylation of the aromatic ring with the electrophilic center of an intermediate.

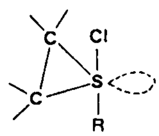
Let us discuss the intermediate structure and general reaction mechanism. Usually, an episulfonium ion of type I (VI) is accepted as an intermediate for the sulfenyl halide addition.[1-3,5] Species of type III (VII), containing the pentacoordinate four-valent sulfur,[25] have also been discussed in some recent publications.[25-29] ‡ The difficulty of an unambiguous representation of this reaction is connected with its two unique and intriguing features. Firstly, the addition reaction of sulfenyl halides occurs with *trans* stereospecificity whose steric course does not depend on the solvent or the olefin structures. *Trans* addition (*diaxial* for cyclic systems) have been found to occur to acyclic,[1-3,5] alicyclic (tetradeuterocyclohexene[33] and its derivatives,[34] and α-cholestene[35]), strained bicyclic (norbornene and its derivatives,[36-38] 7-oxabicyclo[2,2,1]heptenes[39]), and even to olefins which can form resonance-stabilized cations.[13,38] There is only one example of a non-stereoselective addition of sulfenyl halides.[40] § At the same time, the addition of mercuric salts and nitrosyl chloride evidently depend on the olefin structures.[19,41-44]

Secondly, although this reaction usually is considered to proceed by a two-step Ad_E-2 mechanism (route A-C), the mixed addition products (route D) have, for the most part, not been isolated.[1-3,5] This feature makes possible the utilization of acetic acid or acetonitrile as solvents for the sulfenyl halides additions despite their nucleophilic reactivity. Similarly, the neighboring-group participation to yield cyclic products is extremely rare in the addition of sulfenyl halides.[6-10,48] Skeletal rearrangements (route E) are similarly quite rare in this reaction. (Note that a carbon atom may be considered as a "neighboring substituent."[49])

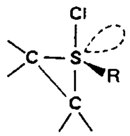
The last feature appears to contradict the assumption that the episulfonium ion I (VI) is an intermediate in the first slow step of the sulfenyl halide addition. We are driven to the conclusion that the realization of a clear-cut two-step addition process suggests that episulfonium ion has to be subject to an attack by the external nucleophiles (routeA-D) which include the solvent or the carbon atom of the migrating substituent (route A-E). The other supporting argument may be extracted from the solvolysis data (Table 1). Taking into account the large driving force of the neighboring RS group participation, it has been proved that the formation of episulfonium ion (VI) in the solvolysis of the compounds containing an RS–C–C–X framework is taking place.[50-52]† The data in Table 1 show that 1,2-aryl migration occurs much more in solvolysis than in the BSC addition under comparable conditions. These data suggest that intermediates of type VI are more polar species than those in the BSC addition. Recently published findings also support this conclusion.[26-28] For example, the addition reaction of the methanesulfenyl tetrafluoroborate is a clear-cut two-step process and the addition of nucleophiles [*e.g.* Cl^-, Br^-, H_2O, CH_3OH, CH_3CN, CH_3COOH, H^-, $(C_2H_5OOC)_2CH^-$] gives a wide range of products of mixed addition.[28]



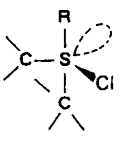
VIIa



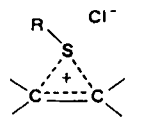
VIIb



VIIc



VIId



XII

We therefore conclude that less polar species like the sulfuran VII or the ion-pair XII may be regarded as intermediates for the BSC addition. It is evident that VI and VII are the limiting cases of a dissociation or a covalent bonding in XII. *We believe that the most reasonable explanation for R–S–X additions is based on the assumption that there exist intermediates (VII, XII or VI) with different S–X bonding.* The inter-

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† *Fahey*[5a] *has written: "The best evidence for stepwise addition via a cationic intermediate would come from the observation of Wagner-Meerwein rearrangement accompanying addition . . ."*

‡ *For a discussion of the geometry of sulfurans see refs. 30-32.*

§ *The abnormal steric course of an addition reaction may sometimes be caused by the thermodynamic control of reaction products. For example, the RSCl addition to dihydropyran occurs with* trans *stereochemistry at low temperature, however, a* trans-cis *rearrangement occurs during an increase in temperature.*[45] *The stabilization of the* cis-*adduct might be due to an anomeric effect.*[46] *We should also mention, that special care should be paid when drawing conclusions regarding the distribution of isomers* (i.e., *those due to Markownikov or anti-Markownikov addition*) *inasmuch as there are many examples of the thermodynamic control of this process.*[3,35,47]

† *An alternative explanation for the formation of the rearrangement products in the solvolysis of IX and X involving phenonium ions is unlikely because neighboring group participation of the aryl groups is substantially less than that of one of the RS groups.*[53]

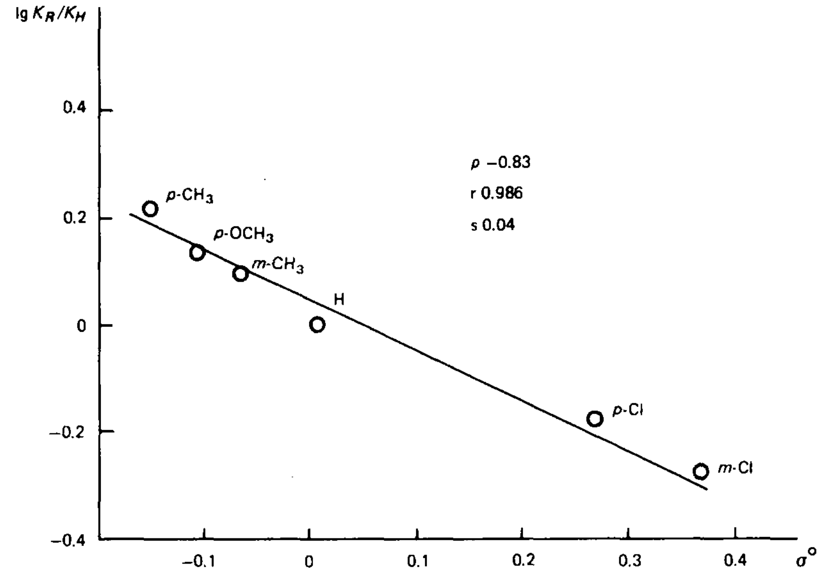


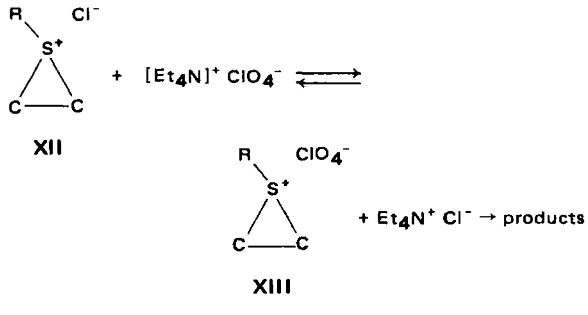
FIGURE I

The rate correlation *vs.* σ^o for the reaction of VIII with BSC in AcOH–CCl_4 (1 : 3) at 25°C

mediacy of an episulfonium ion VI depends on a nucleophilicity of X. The formation of VI occurs with poorly nucleophilic anions like BF_4^- [28] or 2,4,6-$(NO_2)_3C_6H_2SO_3^-$ [26,27] but presumably does not occur if X is a halogen anion. The intermediacy of the sulfuran VII or the ion-pair XII in a sulfenyl chloride addition strongly depends on the solvent used. The intermediate structure is close to VII in non-polar solvents such as CCl_4. Hence the addition in non-polar media proceeds without any competing processes connected with the development of the positive charge on the carbon atoms (routes A-D and A-E). Ion-pair formation may be proposed for the addition in acetic acid as a solvent. The symmetry of the bridged structure XII should depend on substituent stabilization. However, the effect of substitution on the rate of addition should be substantially smoothed if the reaction proceeds *via* ion pair XII rather than *via* pure ion VI. The experimental data are in a good agreement with this conclusion, *i.e.*, there is correlation with inductive substituent constants.

We have also tried to find experimental evidence for ion-pair formation (XII) in the BSC addition. Studies of the "special salt effect" discovered by Winstein and his co-workers[54] proved extremely successful in the investigation of ion pairs in many solvolyses. This effect seems to operate when the solvent separated ion pair is captured by added salt, usually lithium perchlorate, thus eliminating part of the ion-pair return.

We have used the "special salt effect" as a tool to prove ion-pair formation in BSC addition. Tables 1 and 2 show that tetraethylammonium or lithium perchlorate addition sharply raises the yield of the rearrangement products. Table 2 shows the yield of ketones XId and XIe depends on the quantity of added perchlorate salts. Thus we found that the addition of perchlorate salts leads to a drastic change in the distribution of competing products. This may be explained accordingly by the suppression of the return from ion pair XII due to an exchange reaction between two ion pairs.[54] The new ion pair XIII



rapidly breaks down to give rearrangement products owing to the low nucleophilicity of the ClO_4^- ion.*

Regarding the sulfuran structure VII (see ref. 27), MO calculations support structure VIIa rather than VIIb. However, in our opinion the alternative trigonal-

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* *An alternative explanation which invokes phenylsulfenyl perchlorate formation and its subsequent reaction with olefin seems to be much less probable* (e.g., *see ref. 23a*). *Independently from the both alternatives, it is evident that the sulfenyl halide addition proceeds* via *a more polar intermediate when the perchlorate salt is added.*

bipyramidal structures VIIc or VIId are worth considering, inasmuch as a conversion of VII may occur *via* pseudorotation.[55] Structure VIIc satisfies tendencies of both a lone electron pair to occupy the most electronegative biaxial orbital and the other of a chlorine atom to occupy the apical orbital.[31, 32]

In addition both the non-bonded interactions and the angle strain should be less in VIIe than in VIIb. *Trans* addition may be attributed to the rear attack of the carbon atom in the intermediates VII and XII by Cl^- (compare with the ion-pair mechanism described in refs. 5 and 16).*

Experimental Section

The AcOH and CCl_4 were purified[56, 57] and the BSC was prepared according to Almast *et al.*[58] The alkenols VIIIa–d were prepared from isopropenyl lithium and corresponding ketones.[59] Compounds VIIIe and f were obtained analogously: VIIIe, b.p. 109°/3 mm, n_D^{20} 1.5282 and VIIIf, b.p. 109°/2 mm, n_D^{20} 1.5460.

Nmr spectra of IX-XI (CCl_4) and their 2,4-DNPH derivatives (pyridine) were determined on a Varian T-60 spectrometer using hexamethyldisiloxane as an internal standard. Both preparative and thin layer chromatography were done on activity II or III alumina using hexane-ether as an eluant. Yields of ketones XI were measured both by the C=O i.r. band near 1720–1725 cm^{-1} and by weighing of their 2,4-DNPH derivatives whose analytical samples were twice recrystallized from BuOH-AcOEt. All compounds investigated had acceptable elemental analyses.

Reactions of VIII with BSC.

a) To 0.003 mol of BSC in AcOH was added 0.003 mol of VIII in 25 ml of HOAc. After decolorization (15–30 min), the oil precipitated by water was extracted by CH_2Cl_2, washed by Na_2CO_3 and water and then dried and evaporated *in vacuo* at the room temperature. The residue was used for the rearrangement product determination and/or for the isolation of pure IX, X or XI by preparative chromatography.†

b) A mixture of both 50 ml of BSC solution of 0.1–0.15 mol/l and VIII in AcOH–CCl_4 (1 : 3) was kept in dark at 20° till decoloration (40–90 minutes) and worked up as above. The reactions in CCl_4 were carried out similarly.

c) To a 25 ml solution of VIIId (0.14 mol/l in AcOH) and perchlorate salt (see Table 2) was added to 25 ml of 0.14 mol/l solution of BSC and worked up as above. For preparative isolation of XId the concentration of the $Et_4N^+ClO_4^-$ solution was 10^{-2} mol/l.

Solvolysis of adducts IX and X.

The adducts from the addition reactions of VIII with BSC in CCl_4 were used for solvolysis after removing the solvent *in vacuo* without special purification.

a) The solution of 0.01 mol of IX or Xb,d,e, and 0.01 of AcONa in 50 ml of AcOH was heated at 75° for 30 hr. The products were worked up as mentioned above. Analogously the solvolysis was carried out in 90% AcOH. Pure XId and XIe were isolated by chromatography

b) To 20 ml of a 0.25 solution of 2,4-dinitrophenylhydrazine was added to a solution of 0.005 mol of IX or X in 50 ml ethanol and mixture was kept for 3 days.

TABLE 3

Constants and PMR data of the compounds investigated

Compounds	M.p., °C, or ($n_D^{20°}$)	Chemical shifts (δ)[a] $-CH_2-$	 CH_3-C-	 CH_3X
IX, Xb	(1.5985)	3.2s 2.9d, 3.5d J = 14 Hz	1.50s	1.65s
IX, Xd	(1.6029)	3.3s 2.95d, 3.6d J = 14 Hz	1.65s	1.7s
IX, Xe	(1.6045)	3.2s 2.95d, 3.5d J = 14 Hz	1.6s	1.7s
IX, Xf	(1.6041)	3.25s 3.0d, 3.5d J = 14 Hz	1.6s	1.7s
XIa	44–45	3.3s	1.5s	1.75s
XIb	(1.5890)	3.35s	1.55s	1.8s
XId	(1.5950)	3.4s	1.6s	1.85s
XIe	47–48	3.35s	1.56s	1.85s
DNPH-XIb	159–160	3.5d, 3.65d J = 13 Hz	1.69s	1.71s
DNPH-XIc	140–141	3.5d, 3.65d J = 13 Hz	1.69s	1.72s
DNPH-XId	160–161	3.6d, 3.85d J = 12 Hz	1.69s	1.72s
DNPH-XIe	129–131	3.53d, 3.56d J = 14 Hz	1.69s	1.72s
DNPH-XIf	130.5–131.5	3.5d, 3.75d J = 14 Hz	1.65s	1.69s

[a] Aromatic proton signals are in the range of 8–9 ppm for DNPH and 6.5–7.5 ppm for IX, X and XI.

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* *The above-mentioned features suggest the idea of intramolecular attack by* Cl^- *although it has not been proved experimentally. One may assume either an equilibrium of* cis *and* trans *ion pairs* (e.g., *see refs. 5 and 16*) *or an intramolecular chlorine migration to the rear of a carbon atom in VIIc or VIId. This problem deserves additional investigation since the latter process should be symmetry-orbital controlled.*

† *In the reaction of VIIIa an equivalent of AcONa was added before mixing with BSC. Experiments with isolated IX, Xb and IX, Xd show that there are no transformation of the adducts into ketones XI during the work-up procedure.*

Kinetic experiments.

All of the kinetic studies were carried out in a reaction vessel at 25° ± 0.1°. Starting concentrations of reagents were 0.01 mol/l. Samples were withdrawn periodically and analyzed photocolorimetrically using a blue filter. The error of measurement was ±2% ($\alpha = 0.95, n = 5$). Temperature variation of the samples were 0.2°. Good second-order rate constants were found for all alkanols except VIIIa up to 90% completion. Errors were calculated at $\alpha = 0.95, n = 5$ (*cf.* Table 1).

Control runs with the addition of 0.005 mol HCl were carried out to study the possible transformation of VIII in the kinetic experiments. It was found that VIIIb and d did not change in any significant manner as determined by v.p.c. (5% polyethylene glycol adipinate on Chromosorb at 155°). However, VIIIa gives a small quantity of unidentified products. For that reason, kinetic studies of the VIIIa addition reaction were carried out only to 60% completion.

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