Use of $MeNO_2$–$LiClO_4$ in promoting a 1,2-shift in RSCl electrophilic addition to 3,3-dimethylbut-1-ene: reaction course and stereochemistry

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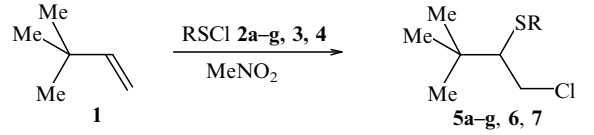
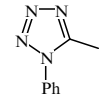
In the Ad_E reaction of RSCl with 3,3-dimethylbut-1-ene the system $MeNO_2$–$LiClO_4$ serves as an efficient promoter of a 1,2-shift which occurs either simultaneously with the electrophilic addition step (π-route) or as a rearrangement of the initially-formed 1,2-adducts (σ-route) and proceeds in a highly stereoselective fashion.

Ad_E reactions of α-branched alkenes, like 3,3-dimethylbut-1-ene **1**, with strong electrophiles are often accompanied by 1,2-shifts and occurrence of the latter is considered to be diagnostic of the intermediacy of carbocationic species.[1] On the contrary **1** reacts with weak electrophiles like RSCl with nearly exclusive formation of unrearranged anti-Markovnikov (aM) 1,2-chlorosulfides[2a] even after addition of a doping system (AcOH–$LiClO_4$).[2b] At the same time it was also observed that preformed episulfonium salts derived from **1** are able to undergo a 1,2-methyl shift [3] which ultimately led to the formation of the product of intramolecular cyclization, the 3,4,4-thiochromane derivative (*vide infra*).

Various Lewis acid-catalysed reactions are also known to be promoted by $LiClO_4$.[4] In particular, the course of RSCl addition at the double bond of strained bicyclic alkenes might be significantly affected if the reaction is carried out in $MeNO_2$–$LiClO_4$ and under these conditions extensive formation of the rearranged products is observed.[5] Here we report that this system reveals the unique property of triggering 1,2-shifts in RSCl addition to **1** and present some evidence about the course and stereochemistry of the observed transformations.

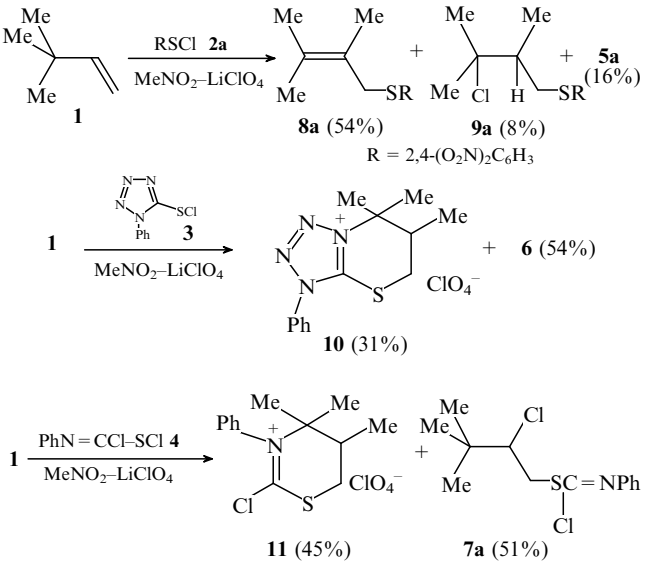
Addition of a series of arylsulfenyl chlorides **2a-g**, 1-phenyltetrazolyl-5-sulfenyl chloride **3** and *N*-phenyliminochloromethanesulfenyl chloride **4** to the double bond of **1** in neat $MeNO_2$ proceeded uneventfully and gave nearly quantitative yields of aM 1,2-adducts **5a-g**, **6**, **7** †,‡ (Scheme 1) regardless of the electronic and steric peculiarities of the substituents at the sulfenyl centre (*cf.* data in refs. 2*a,b*, 3).



R = 2,4-$(O_2N)_2C_6H_3$ (**2a, 5a**); Ph (**2b, 5b**);
4-MeC_6H_4 (**2c, 5c**); 4-ClC_6H_4 (**2d, 5d**);
2-$O_2NC_6H_4$ (**2e, 5e**); 4-$O_2NC_6H_4$ (**2f, 5f**);
2,4,6-$Me_3C_6H_2$ (**2g, 5g**);
PhN=C(Cl) (**4, 7**);  (**3, 6**)

Scheme 1

A strikingly different pattern of reactivity was observed when the same set of reactions was carried out in $MeNO_2$ in the presence of 5 equiv. of $LiClO_4$. Under these conditions the addition of **2a** to the double bond of **1** was accompanied by a 1,2-methyl shift and led to the formation of compounds **8a** and **9a** as the major products§ (Scheme 2). Reaction of **1** with sulfenyl chlorides **3** and **4** in this system also gave substantial amounts of the rearranged products, the respective thiazinium salts **10** and **11.**¶



Scheme 2

Control experiments have shown that under similar conditions the preformed 1,2-adducts **5a**, **6**, **7** do not undergo 1,2-shifts and hence the products **8a**, **10**, **11** are formed in the course of the Ad_E reaction (π-route).

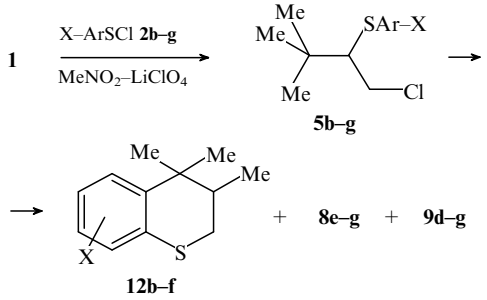
Interaction of **1** with **2b–g** in $MeNO_2$–$LiClO_4$ also proceeds with 1,2-shifts and resulted in the formation of thiochromane derivatives **12b–f** and/or rearranged acyclic adducts **8e–g**, **9d–g** (Scheme 3).†,¶

However, NMR-monitored experiments demonstrated that these reactions involve the initial rapid formation of 1,2-adducts **5b–g**, followed by a slow transformation of the latter into rearranged products (σ-route). As one might expect, this rearrangement proceeded rather easily for **5b,c**, while the presence of electron-withdrawing groups in the benzene ring of adducts **5d–f** sharply reduced both the rate of rearrangement and yields of the final products.*

The rearranged products **10–12** revealed a well-expressed AB-pattern of splitting in the ^1H NMR spectra for the CH_2S-fragment. This peculiarity presented a unique opportunity to

† All reactions were carried out at 20 °C.
‡ The structure of adduct **5a** was established by X-ray analysis; aM structure for other 1,2-adducts was ascertained by the comparison of their ^1H and ^{13}C NMR data with those for **5a**.

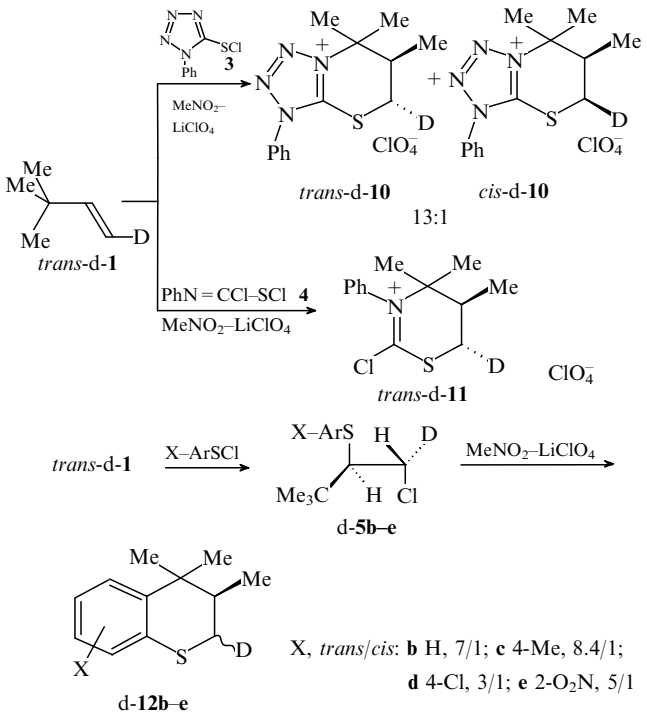
§ Adduct **9a** arose due to the secondary reaction of HCl addition to **8a**, as shown by a special experiment.
¶ A consistent spectral (NMR, MS) and analytical data were obtained for all rearranged products.
* In all cases a minor amount (up to 5%) of the respective M adducts were also formed. Rearrangement of **5g** proceeds with extensive decomposition and gives $(MzS)_2$ in 66% yield.



X	Time / h	Product yield (%)		
		12	**8**	**9**
H (**5b**)	18	72	–	–
4-Me (**5c**)	18	77	–	–
4-Cl (**5d**)	24	40	–	5
2-O_2N (**5e**)	96	42	5	29
4-O_2N (**5f**)	168	5	5	24
2,4,6-Me_3 (**5g**)	5	–	5	12

Scheme 3

investigate the stereochemistry of 1,2-methyl shifts involved in the formation of these adducts. To resolve this problem the reactions mentioned above were carried out with *trans*-1-deuterio-3,3-dimethylbut-1-ene, *trans*-d-**1**. ^{1}H NMR data including observation of NOE, were employed for stereochemical assignments. It was found that a highly stereoselective (for reaction with **3**) or even stereospecific (for reaction with **4**) 1,2-methyl shift took place in the course of



Scheme 4

formation of the rearranged products, d-**10** or d-**11**, respectively, *via* a π-route. Predominant or even exclusive formation of the isomer with a *trans*-oriented methyl group and deuterium atom was observed. Rearrangement of the preformed 1,2-adducts d-**5b–e** into thiochromanes d-**12b–e** (σ-route) also proceeded with significant stereoselectivity. The latter was shown to depend upon the nature of the substituent at the sulfur centre (Scheme 4).

It is to be emphasized that in all cases the Ad_E reaction of *trans*-d-**1** with RSCl to give adducts d-**5b–e** occurred cleanly as a stereospecific *trans* addition to the double bond of *trans*-d-**1**.

The observation of 1,2-methyl shifts in the above reactions suggests the formation of highly polarized or even ionic intermediates in the product-determining step. High stereoselectivity of the shifts observed for the rearrangement of the preformed aM adducts **5b–e** into the cyclic products **12b–e** should be taken as unambigious evidence in favour of a mechanism involving the intermediacy of the bridged species like episulfonium salts[3] which undergo subsequently an intramolecular opening more or less concerted with 1,2-methyl migration.[††] A similar mechanism might be operative in a π-route leading to an almost stereospecific formation of products d-**10** and d-**11** though one cannot exclude an alternative which envisages a nearly synchronous formation of the C–S bond and a 1,2-methyl shift in the initial Ad_E step. Additional experimental studies are most certainly warranted in order to elucidate the relative importance of various factors affecting the reaction course and thus to arrive at a more consistent formulation of its mechanism.

It is also to be mentioned in conclusion that while the ability of $LiClO_4$ to serve as a specific Lewis acid catalyst is a well-documented phenomenon,[4] the result of this study clearly demonstrate that its activity[‡‡] can be further enhanced by use of a highly-polar solvent like $MeNO_2$.

The preparative ramifications of this finding are currently being investigated by our group.

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[††] A nearly stereospecific 1,2-methyl shift was also observed for the rearrangement of *S*-methylthiiranium salt obtained from *trans*-1,2-di-*tert*-butylethylene into the respective thietanium salt under the 'long-life conditions'.[6]

[‡‡] It is also noteworthy that the utilization of $Mg(ClO_4)_2$ gave results nearly identical to those described above for $LiClO_4$, while no rearranged products were formed for the reaction of **1** with RSCl in the presence of Bu_4ClO_4 (*cf.* data on the effect of cations on the Lewis acid activity of perchlorates in ref. 7).