Tetrahedron. Vol. 31, pp. 2948 to 2952. Pergamon Press 1975. Printed in Great Britain

NEW METHOD FOR INCREASING OF ELECTROPHILICITY OF WEAK ELECTROPHILES IN ADDITION REACTIONS

WAGNER-MEERWEIN REARRANGEMENT IN A REACTION OF 2,4-DINITROBENZENESULFENYL CHLORIDE WITH NORBORNENE

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(*Received in UK* 29 *May* 1975; *Accepted for publication* 30 *June* 1975)

Abstract—A new method for increasing of the effective electrophilicity of weak electrophyles in addition reactions has been developed, using as a model reaction the addition of 2,4-dinitrobenzenesulfenyl chloride to norbornene. The features of this reaction and some general problems of an electrophilic addition are discussed.

The addition of electrophilic reagents to a double bond[1] can provide a great number of types of reactivity including (a) the normal trans-addition of the electrophile moieties, (b) skeletal rearrangement of the Wagner-Meerwein type, (c) mixed addition of the electrophile and external nucleophile with or without rearrangement, (d) different types of proton elimination, etc. One of the most popular (though not well supported) mechanisms suggests that an "onium ion" type of intermediate is involved in the addition process. More modern rationalizations of this reaction include other intermediate species, such as π-complexes,[2] polyvalent species,[2,3] ion pairs,[1,4,5] etc.

However all of these mechanisms have one feature in common: in all development of the positive charge(s) on the carbon atom(s) in the intermediate is accepted, because the carbenium-ion type of rearrangement often occurs in addition reactions. This situation allows a rough division of the whole number of electrophiles into two groups: (a) strong electrophiles, which generate a relatively large positive charge on the carbon atom/s and (b) weak electrophiles, which generate small one/s. The first group embraces such reagents as chlorine, hydrogen halides, peracids, etc. Addition of these reagents is often carried out with some kind of skeletal rearrangement. The second group includes such reagents as mercury salts, sulfenyl halides, nitrosyl halides, etc. which give the rearranged products only in the extremely rare cases—for special models of unsaturated compounds†.[2,6,7]

One problem in principle may be formulated as a question: is it possible to increase the electrophility of weak electrophiles? The importance of this problem is evident: if this were possible, the whole spectrum of new compounds including the rearranged structure would be available.

One approach is evident and relates to the increasing of polarization of the X-Y bond of the electrophilic reagent, e.g. with addition of reagents forming complexes, such as Lewis acids. The wide synthetical application of the strong polarized complexes ($RS^+BF_4^-$, $Ac^+BF_4^-$, $NO_2^+BF_4^-$, etc.) in electrophilic addition has been elaborated by Smit *et al.*[8,9] This approach resembles the M^+-S_N1 and M^+-S_N2 processes in nucleophilic substitution.[10]

Recently, we have developed a new method for increasing electrophilicity due to the addition of strong electrolytes.[2,11] The addition of the salt shifts the polarity of the intermediate (e.g. it leads to the formation of new ion pairs) and, as a result, the reaction proceeds via more polar species (*vide infra*). This approach resembles "the special salt effect" in solvolysis.[12]

Thus, the work reported in this paper was directed towards developing a new method for increasing the electrophilic reactivity of "weak electrophiles". The addition of dinitrobenzenesulfenyl chloride (1) to norbornene (2) was chosen as the model reaction (see preliminary communication[13]). The reason for this choice was the following. First of all, addition of sulfenyl halides to the double bond proceeds with Wagner-Meerwein rearrangement only in extremely rare cases. Moreover, this reaction usually proceeds via addition of the fragments of the initial sulfenyl halide and the nucleophilic participation or the addition of the external nucleophile is also extremely rare‡. Recently we have discussed the unique features of this addition reaction and suggested some evidences of the formation of sulfurane as the intermediate in non-polar media.[2] Secondly, the addition of 2,4-dinitrobenzenesulfenyl chloride to norbornene has been previously studied by Kwart and Miller, who found that this reaction occurred without the Wagner-Meerwein rearrangement.[14] Taking these points into account, we can say that this reaction seems to be a very reasonable model for the above-mentioned investigation.

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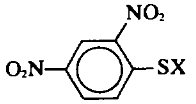
†Of course, this division is rough and conventional; many "borderline" cases may exist. However, this definition is very useful in the literature.[1]

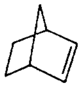
‡This situation allows use of the nucleophilic solvents (AcOH, CH_3CN, etc.) for this reaction.

RESULTS

First, let us briefly consider the results of Kwart and Miller.[14] These authors have found that addition of **1** to norbornene(**2**) gives two isolated products, namely trans-adduct **3** and nortricyclene **4**. The ratio of the two products was found to be dependent on the solvent. In non-polar solvents (CCl_4, dichloro- and dibromoethane) at a temperature below 50° trans-adduct is strongly predominant. The use of the considerably more polar acetic acid (temperature 26°) resulted in a large decrease in the ratio of **3** to **4**. The authors have observed formation of a significant amount of oily residue of undetermined nature in the last case. We have to emphasize that neither rearranged product **5** nor acetates **6** have been detected, probably because the american authors[14] have made use of a ruse but not a very efficient method of separation (flotation of the crystal solid).

We have reinvestigated these results, using the effective method of separation by chromatography. We have found, that chloride **3** was really the main product in CCl_4.


1: X = Cl
7: X = OCOCH$_3$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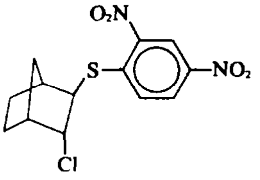
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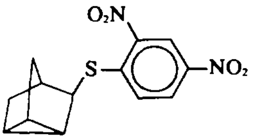
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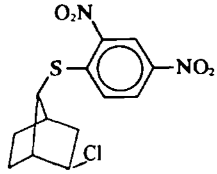
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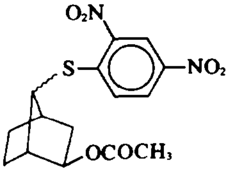
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The main products were chloride **3** and nortricyclene **4** in acetic acid at 25°; however we could isolate the small quantity of the acetates **6** (Table 1). The reaction in acetic acid at 55–60° leads to different products: the rearranged chloride **5** (25% yield) have been isolated together with **3** and **4** (Table 1).

The structures of the compounds obtained have been determined by NMR spectra. The spectrum of the chloride **5** shows the singlet at δ 3·35 ppm ($W_{1/2}$ 3 Hz)(H–C–S–) and quadruplet at δ 3·96 ppm (coupling constants about 7·5 and 5 Hz) (H–C–Cl), which indicates the 7-th-position of sulfur containing substituent and 2-*exo*-position of Cl atom.[15] It is very difficult to separate the mixture of **3** and **4**. However the quantitative determination of these compounds can be easily accomplished using the NMR spectra, namely, singlet at δ 3·25 ppm (H–C–S for **4**) and multiplet at δ 3·98 ppm (for **3**). The signals were attributed by using spectra of pure samples of **3** and **4**.

Detailed study of "acetate" **6** (m.p. 105–106°) has showed that it is the mixture of two isomers, which have been separated with chromatography. One isomer **6a** has m.p. 129–130°; NMR spectrum of **6a** shows a singlet at δ 3·36 ppm (H–C–S) and triplet at δ 4·65 (H–C–O, the width over extreme peaks is 10·7 Hz). The second isomer (**6b**) has m.p. 126–127° and shows singlet at 3·65 ppm (H–C–S) and quadruplet at δ 4·7 ppm (H–C–O, the width over the extreme peaks is 11·5 Hz) in its NMR spectrum. It is evident that both acetates **6** contain the R-S-group in 7-position, because the H–C–SR signals are sharp singlets. The width of the H–C–O signals, which is the $|J_{AX} + J_{BX}|$, points out the 2-*exo*-position of acetoxy groups in both isomers.[15] The degeneration of this signal into the triplet in the spectrum of **6a** is not probably due to the equality of coupling constants, but due to $\Delta\delta_{AB} \sim 0$. Thus, the isomers of **6** have the 2-*exo* acetoxy groups and differ with the orientation of 7-RS groups. The 7-synisomer formation is due to the occurrence of "normal" Wagner-Meerwein rearrangement; the *anti*-isomer formation is due to the additional 2,6-hydride shift in a course of the rearrangement (see, for example[16]).

We also investigated the addition of 2,4-

Table 1. Yields of the products in addition reaction to norbornene

Electro-phile	Solvent	Temp.	$\frac{LiClO_4}{ArSX}$	Yield (%)					
				3	**4**	**5**	**6a** (m.p. 129–130)	**6**	**6b** (m.p. 126–127)
1	$CH_2Br–CH_2Br$	50	—	70	10*	—	—		—
1	CH_3COOH	25	—	75 (1:3)		—		7	
1	CH_3COOH	60	—	55 (1:3)		25		3	
1	CH_3COOH	60	2:1	5 (1:1·5)		trace	60		20
7	CCl_4	25	—	—	30	—	—		—
7	CH_3COOH	25	—	—	30	—	7		20
7	CH_3COOH	25	3:1	—	10	—	50		25

*Ref. 14.

dinitrobenzenesulfenyl acetate (**7**) to norbornene. This reaction in CCl_4 gives pure nortricyclene **4** and mixture of **4** and **6** in acetic acid (Table 1). Bis(2,4-dinitrophenyl)disulfide has also been isolated in this addition reaction.

After that, we began to study the investigation of the influence of the addition of $LiClO_4$ on a ratio of the reaction products. We have found, that addition of **1** to norbornene in the presence of $LiClO_4$ in acetic acid occurred in a completely different manner, and the rearranged acetates **6** were the main products (80% yield, Table 1). The yields of rearranged acetates **6** depend on the quantity of $LiClO_4$ added. Analogously, the addition of $LiClO_4$ in the reaction of 2,4-dinitrobenzenesulfenyl acetate with norbornene also changes the ratio of products increasing the yield of acetate **6a** (Table 1). Finally, the special experiments showed, that acetates **6** were not produced in solvolysis of chlorides **3** and **5** in acetic acid in the presence of $LiClO_4$ under the conditions chosen for the addition reactions.

DISCUSSION

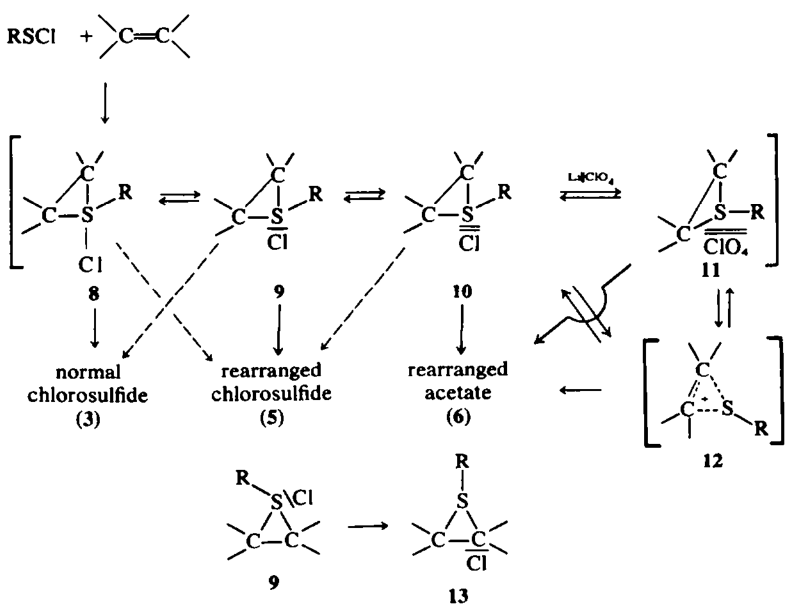
In this paper we must emphasize two main results obtained: (a) an addition of **1** to norbornene is unprecedently dependent on the temperature[†] and can proceed with Wagner-Meerwein rearrangement, (b) without the addition of salts only corresponding chlorides are formed even in Wagner-Meerwein rearrangement process, and the participation of external nucleophile (acetic acid) is negligible, (c) the addition of the strong electrolyte to the reaction ($LiClO_4$) drastically shifts the polarity of the intermediate(s) and, thus, completely changes the nature of the product obtained.

Let us consider briefly the mechanism of addition of sulfenyl halides. Recently we have summarized and produced new evidence that (i) addition of sulfenyl halides occurs as a two-step process and Wagner-Meerwein rearrangement occurs in the second, non-rate-limiting step, (ii) a sulfurane (**8**) is an intermediate in non-polar solvents[‡] and (iii) the separated ion-pair is involved in this addition in polar solvents.[2] The general mechanism is shown in Scheme 1. To keep the discussion as simple as possible, we will suppose that normal *trans*-adduct **3** and rearranged chloride **5** are produced from sulfurane **8** and intimate ion-pair **9** respectively. The separated ion-pair **10** produces either **5** or the acetate(s) **6** after an exchange with solvent (CH_3COOH).[§]

First let us consider the reaction without the addition of the salt. If we accept that the ratio of products **3** and **5** depends on the ratio and reactivity of intermediates **8** and **9**, we must conclude that these parameters are extremely sensitive to temperature. Second, it is important to underline that chlorides (**3** and **5**) but not the acetates (**6**) have been obtained mainly in the reaction.

The unrearranged *trans*-acetate has not been observed in any case either this is a clear evidence against the bare episulfonium ion **12** as an intermediate in these processes. Thus neither the rear-side attack of the C atom when going from **8** to **3** (*trans*-configuration!) nor the rearrangement in going from **9** to **5** (or **10** → **5**) includes the complete dissociation of S–Cl bond.[‖]

Hence one question may be posed: where is the Cl atom taken from? This is a general and important but, to our knowledge, completely non-investigated problem in the electrophilic addition. The formation of *trans*-products is usually explained in terms of the rearrangement of cissoid ion-pair (**9**) into the transoid one **13** (Scheme 1) with the sliding of the anionoid atom or group from the frontal side



Scheme 1.

[†] Professor V. A. Smit kindly informed us of his having observed the extremely sharp dependence of the addition of $RSBF_4$ to *t*-butylethylene on temperature.[9]

[‡] Recently analogous selenurane has been determined in addition reaction by the NMR-technique.[3]

[§] Of course, each of these species can have a number of types of reactivity (dotted lines on Scheme 1). The strong division of types of reactivity, made above, seems to be very reasonable in order to simplify the discusion, especially in the absence of fine experimental data on the matter.

[‖] Evidently, this rearrangement closely resembles the ones with "internal return" of the ion-pair in solvolysis (see, for example Ref. 17).

of an intermediate to the rear-side.[1,4,5] If this mechanism really operates, the X and Y moiety in adduct must be accepted from the same molecule of the electrophilic reagent, as shown:

$$2\,C{=}C + X\text{-}Y + X^*\text{-}Y^* \rightarrow X\text{-}C\text{-}C\text{-}Y + X^*\text{—}C\text{-}C\text{-}Y^*$$

where asterisks are placed to individualize the X–Y molecules. The "onium-ion" mechanism, or the one with the exchange between the separated ion-pairs permits the introduction of anion from the other molecules of electrophilic reagent. The formation of both the rearranged and non-rearranged chlorides offers evidence in favour of intramolecular process for the transformation of sulfurane **8** into **3** and intimate ion-pair **9** into **5**.†

Let us consider now the influence of the addition of a strong electrolyte. The results obtained present clear-cut evidence that addition of the $LiClO_4$ leads to the strong increase of the effective electrophilicity of the reagent used, which, in turn, leads to (a) formation of only the rearranged products and (b) nucleophilic participation of the external nucleophile(solvent) in the final step of the reaction. We did not experimentally investigate the mechanism of the $LiClO_4$ participation in the present study. However, some principal points should be mentioned. Thus, the action of the salt added is not connected with the increase of the RS–Cl bond polarity in the initial reagent and, hence, with the transformation of the reagent into more polar species, as for example into acetate **7**. The experiments with **7** (*vide supra*) clearly showed that this reagent gives different reaction products with and without $LiClO_4$. Thus, the salt participation is effective at intermediate steps of the reaction. In the absence of special investigation one can only assume that the mechanism operating here resembles the one proposed for "the special salt effect" in solvolysis[12] (see, however,[20]). The addition of $LiClO_4$ suppresses internal return in the solvent-separated ion-pair **10** (namely **10**→**9** and **10**→**5** processes), due to the exchange reaction between the **10** and $LiClO_4$. Owing to the low nucleophilicity of the perchlorate ion, the new ion-pair **11** is more polar than **10** and has the increased positive charges on the C atoms, which can be compared with the ones on the C atoms of the bare episulfonium ion **12**. Thus new ion-pair **11** is rapidly attacked by the nucleophilic solvent to produce the rearranging acetates **6**.

CONCLUSION

In this work we have investigated (partially reinvestigated) the model reaction of 2,4-dinitrobenzenesulfenyl chloride with norbornene. The main result may be summarized as follows:

(1) In contrast to published data, this reaction can occur with the Wagner-Meerwein rearrangement to give the chloride **5**. The ratio of the rearranged and non-rearranged (**3**) products was found to depend on the temperature and solvent used. Only a small quantity of acetates has been isolated in acetic acid.

(2) We proposed a new method for increasing the effective electrophilicity of "weak electrophiles" in the addition reactions by means of adding strong electrolytes to the reaction mixture. Application of this method to the reaction investigated was also successful.

The study of the scope and limitation of this method, its synthetical utility and extension to other classes of "weak electrophiles" and substrates (aromatic and cyclopropanic hydrocarbons, etc.) is now actively underway.

EXPERIMENTAL

The acetate **7** was prepared according to Ref. 21. AcOH was purified according to Ref. 22. Both preparative and TLC was done on alumina (activity II) or silica gel A40/100 M. IR spectra were recorded on UR-20 instrument. PMR spectra were recorded on Varian C–60–H or X–100–15 spectrometers with hexamethyldisiloxan as the internal standard.

Addition of **1** *to norbornene*

(a) A soln of **1** in 20 ml AcOH was added to a stirred soln of **2** (0·85 g) in 10 ml AcOH. The mixture was stirred for 8 hr, poured in 100 ml water, extracted with $CHCl_3$. The extracts were dried over Na_2SO_4 the solvent was removed and the residue was chromatographed on alumina (ether-hexane 1 : 1) to give (i) the mixture of **3** (R_f 0·6) and **4** (R_f 0·5) (1·9 g, 74%, ratio of **3**–**4** is 1 : 3), m.p. 123°; (ii) acetates **6** (0·2 g, 7%), m.p. 105–106° (from EtOH).‡

(b) A soln of **1** (3 g) in 15 ml AcOH was added to a stirred soln of **2** (1·2 g) in 35 ml AcOH at 55–60°. The mixture was stirred 8 hr at 55–60° and poured in 150 ml water. The analogous workup gave 2·15 g (55%) of mixture of **3** and **4** (1 : 3), 1·09 g (25%) of **5** (R_f 0·32), and 0·13 g (3%) of **6** (R_f 0·25), m.p. 105–106° (from EtOH). Analytical example of **5** had 172–172·5° (from CCl_4) (Found: C, 47·20; H, 4·00. $C_{13}H_{13}ClN_2O_4S$ requires: C, 47·49; H, 3·98%).

(c) A soln of **1** (4 g) in 30 ml AcOH was added to a soln of **2** (1·6 g) in 40 ml AcOH and the mixture was refluxed 8 hr. The ppt of bis - (2,4 - dinitrophenyl) - disulfide (1·84 g, 57%) was filtered off, and the analogous workup of filtrate gave 1·1 g (20%) of mixture of **3** and **4** (1 : 3), m.p. 127–128°, 0·58 g (10%) of **5**, 0·16 g (3%) of acetates **6**, m.p. 105–106° and 0·18 g of unidentified compound, m.p. 164–164·5°.

(d) Anhydrous $LiClO_4$ (3·2 g) was dissolved in 35 ml AcOH at 40°, 1·6 g of **2** was added and then a soln of **1** (4 g) in 15 ml AcOH was added at 55–60°. The mixture was stirred 8 hr at this temp and analogous workup gave 0·17 g (4%) of mixture of **3** and **4** (1 : 1·5); 0·01 g of **5**, 4·9 g (80%) of acetates **6** (R_f 0·25), m.p. 105–106° and 0·28 g of the unidentified compound, m.p. 164–164·5°. Analysis of acetates **6** mixture gave; (Found: C, 51·08; H, 4·68. $C_{15}H_{16}N_2O_6S$ requires: C, 51·13; H, 4·54%). Acetates **6** were separated with column chromatography on silica gel (hexane ethyl acetate 3 : 1). 4·9 g of acetates **6** mixture gave 3·6 g (60%) of acetate **6a**, m.p. 129–130 (from EtOH), R_f 0·38 ("siuful" plates) and 1·17 g (20%) acetate **6b**, m.p. 126–127° (from EtOH–AcOEt), R_f 0·45 ("Silufol" plates).

Addition of 2,4-dinitrobenzenesulfenyl acetate (7) *to norbornene*

(a) A soln of 0·33 g of **2** and 0·9 g of **7** in 150 ml of CCl_4 was

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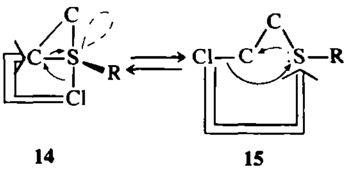
† If we accept that process sulfurane→*trans*-adduct is synchronous, then it must be controlled with orbital symmetry (electronic effect) because the observed transformation of **8** into **3** is evidently a non-least-motion pathway; hence it is not favored on steric grounds. Recently Epiotis revealed[19] that configuration interaction was in principle able to change the stereochemistry of 4n synchronous processes, including the nucleophilic substitution.



14 **15**

The reverse process **15**→**14** is relative to the reactions of the insertion of carbenes into C–X bond which proceed with retention of the configuration. If the **15**→**14** reaction is four-electron process, we may speculate, that configuration interaction can change its stereochemistry to give the *trans*-process (reverse **14**→**15** process must have the same stereochemistry taking into account the microreversibility principle). Evidently, this problem is worthy of special theoretical analysis.

‡ In some experiments a small quantity of unidentified compound, m.p. 164–164·5° (R_f 0·25 in $CHCl_3$) has also been isolated.

stirred 8 hr at 20° in darkness, the solvent was removed *in vacuo* and residue was chromatographed on silica gel (hexane/EtOAc 3:1) to give 0·3 g (30%) of **4**, m.p. 144–145·5° (from EtOH), R_f 0·6 (Found: C, 53·33, H, 4·18, $C_{13}H_{12}N_2O_4S$ required: C, 53·42; H, 4·14. Lit.[14] m.p. 142·8–144°. Additionally 0·6 of bis-(2,4-dinitrophenyl)disulfide has been isolated.

(b) A soln of **2** (0·33 g) and **7** (0·9 g) in 50 ml AcOH was stirred 12 hr at 20° in darkness and analogous workup gave 0·28 g (28%) of **4**, 0·08 g **6a**, m.p. 128–130° (R_f 0·38, "Silufol" plates), 0·23 g (19%) of **6b**, m.p. 126–127° (R_f 0·45, "Silufol" plates), 0·1 g of unreacted **2**. Extraction of adsorbent with $CHCl_3$ gave additionally 0·21 g of bis(2,4-dinitrophenyl)disulfide.

(c) A soln of **2** (0·33 g), **2** (0·9 g) and $LiClO_4$ (1·3 g) in 50 ml AcOH was stirred 8 hr to give 0·12 g (12%) of 4, 0·59 g (48%) of **6a** and 0·31 g (28%) of **6b**.

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