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

REACTIONS OF 2,4-DINITROBENZENESULPHENYL CHLORIDE WITH NORBORNENE AND DIMETHOXYBENZONORBORNADIENE IN FORMIC ACID

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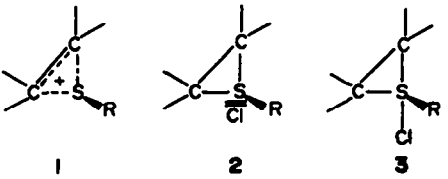
Abstract—The effective electrophilicity of 2,4-dinitrobenzenesulphenyl chloride in its addition to norbornene and dimethoxybenzonorbornadiene in formic acid has been studied.

The electrophilic addition of sulphenyl chlorides to unsaturated compounds has been extensively investigated and reviewed.[1-3] These reagents belong to the group of weak electrophiles: a development of the positive charge(s) on the carbon atom(s) in the intermediate is relatively small, and hence the addition of sulphenyl chlorides is accompanied by rearrangement only in rare cases.[2-4] The outstanding feature of these reactions is the addition of the fragments of the initial sulphenyl halide; the mixed addition products via a participation of the external nucleophile have, for the most part, not been isolated. This permits the utilization of acetic acid or acetonitrile as solvents for the sulphenyl halide addition despite their nucleophilic reactivity. Usually, an episulphonium ion of type 1 is accepted as an intermediate in these additions.[1,3] However we have summarized recently the evidence that the addition proceeds via intermediates like the ion-pair, 2, or the sulphurane, 3, in the media with low ionizing power (CH_3COOH) or in non-polar solvents (CCl_4).[2,3]



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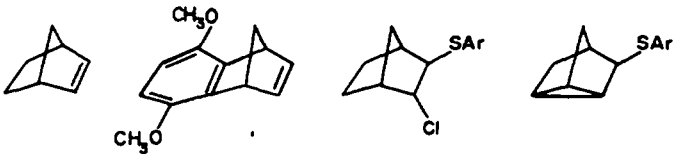
One of the most important synthetical problems with electrophilic additions is to increase effective electrophilicity of weak electrophiles. The successful realization of this problem would permit us to expand the scope of these reactions and the whole spectrum of new compounds including the rearranged structures would be available. In application to the sulphur containing electrophiles there exists 2 methods of the increasing of effective electrophilicity. One method[4-8] consists of the utilization of strongly polarized complexes of type RS^+X^- in addition reactions. The other method has been elaborated by Zefirov, Bodrikov and co-workers,[2,3,9] and is based on the participation of the ion-pairs, 2, in the addition of sulphenyl halides and involves a strong increase of the effective electrophilicity of the reagent used by the addition of a strong electrolyte ($LiClO_4$) to the reaction mixture. The first method resembles the M^+-S_N1 and M^+-S_N2 processes in nucleophilic substitution[10] and the second one resembles "the special salt effect" in solvolysis.[11]

However one may suggest a third method of increasing the effective electrophilicity of weak electrophiles in electrophilic additions which consists in the application of the solvents with the high ionizing power, promoting the dissociation of either the reagent or the other covalent intermediates. Again by analogy with solvolysis one may choose the solvent(s) which either promotes the transformation of the S_N2 process into S_N1 or sharply accelerates the S_N1 solvolysis (e.g. the solvents with large constant Y of Winstein-Grunwald[12]). Although at first sight this approach seems obvious and even trivial, its realisation namely for the addition reactions of sulphenyl halides and weak electrophiles in general is not an easy problem. First, the choice of such solvents is sharply restricted in general. Secondly, some of them can react with sulphenyl halides which also restricts the possibilities. For example it has been documented that sulphenyl chlorides react with alcohols[13] and formic acid.[14] Furthermore, this approach fails sometimes due to the specificity of the addition mechanism. For example, the addition of NOCl to norbornene in formic acid proceeds with the formation of "normal" adduct and the formic acid does not influence the reaction.[15]

In this paper we have studied the applicability of the third method for the two model addition reactions of 2,4-dinitrobenzenesulphenyl chloride (DNBSC) to the norbornene 4 and dimethoxynorbornadiene 5. The choice of these model reactions is due to the knowledge of the product distribution in usual conditions,[3,16] which permits us to compare the effective electrophilicity in the different conditions.

RESULTS

It has been shown[3] that reaction of DNBSC with norbornene proceeds (a) without Wagner–Meerwein



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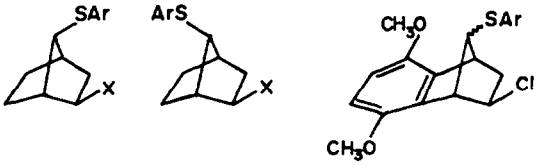
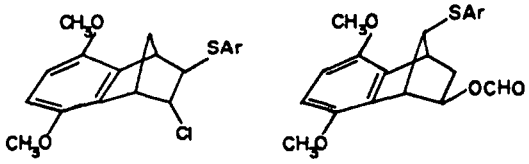


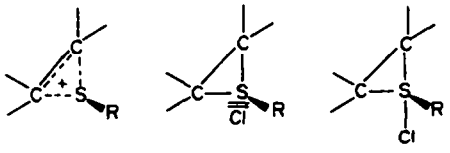
8: X = Cl **10**: X = OAc
9: X = OAc **14**: X = OCHO
13: X = OCHO **17**: X = OH
15: X = OH

11



12 16

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



1 2 3

rearrangement in CCl_4 and in CH_3COOH (20°) to give in last case the mixture of chloride **6** and nortricyclene **7**; (b) to give 25% of rearranged chloride **8** in CH_3COOH (60°) together with 75% of mixture of **6** and **7**; and (c) to give the mixture of rearranged acetates **9** and **10** in CH_3COOH (60°) in presence of $LiClO_4$. The addition of DNBSC to olefin **5** proceeds to give (a) the mixture of chlorides **11** and **12** (with the ratio 1:5) in CCl_4 and (b) the rearranged chloride **11** (42% at 25° and 63% at 60°) in CH_3COOH.[16] We have to emphasize that *only rearranged chlorides* **8** *and* **11** *have been observed in* CH_3COOH *as a solvent*; the formation of *rearranged acetates* **9** and **10** has been observed only in presence of perchlorate salts.

In sharp contrast with these observations we have found that the addition of DNBSC to the norbornene in HCOOH at 20° proceeds to give the *rearranged formates* **13** (syn-, m.p. 140–140.5°) and **14** (*anti*-, m.p. 118–119.5°) (total yield 50%) together with small quantities of **6**, **7**, and nonidentified high-melting products, which are probably due to the partial destruction of DNBSC. The yield of formates depends on temperature decreasing to 9% at 60°. The addition of 0.5 mol of $LiClO_4$ led to a small increase of yield, but the substantional quantity of $LiClO_4$ (up to 2 mol) sharply decreased the yield. The formation of the formates **13** and **14** is not due to the solvolysis of chlorides **6** and **8**. In every case we have isolated variable amounts of rearranged oxycompound **15**; however its formation is probably due to the workup procedure.

The structures of the formates obtained have been determined by PMR spectra. Both formates **13** and **14** have the signal of H–CO with the width over extreme peaks equal 10.5 Hz which point to the 2-*exo*-position of formyloxy groups in both isomers. The signals of H–C–S protons are the singlets with δ 3.27 (**13**) and 3.60 (**14**) ppm, which indicates the 7-position of sulphur containing substituent. Recently we have obtained the rearranged acetates **9** and **10** which structures have been determined by analogous PMR arguments.[3] The choice between *syn*- (**9**) and *anti*- (**10**) isomers has been made by X-ray analysis of the structure of the *anti*-isomer **10**.[17] A low-field shift of H_7 in *anti*-isomer (3.65 ppm in **9** as compare with 3.36 ppm in **10**) permit us to use this difference as a diagnostic tool for the configurational assignment. Thus we suggest the *syn*-configuration for the formate **13** with up-field shift of H_7 and vice versa. Additionally the structures of **13** and **14** has been proved by chemical correlation with acetates **9** and **10** correspondingly after the hydrolysis and acetylation.

The reaction of DNBSC with **5** in HCOOH at 20° proceeds to give 70% of formate **16** together with 27% of rearranged chlorosulphide **11**. Addition of $LiClO_4$ does not substantially influence the course of reaction (54% of **16** and 27% of **11**). The PMR spectra of **11** and **16** contain the signal of protons of CH_2 group which can be interpreted as the AB part of ABX system with additional coupling constant of *exo*-proton due to the $H_{3\text{-exo}}$–H_4 interaction. These PMR data indicate the rearranged structures both **11** and **16**. The H–C–S and H–C–Cl signals for **11** are masked by the CH_3O-signals, which does not permit us to ascribe *exo*- or *endo*-

configuration of chlorine. However the PMR spectrum of **16** contains the quadruplet of H–C–O proton (δ 4.25 ppm) with the width over the outermost peaks 11.8 Hz which is $|J_{AX}+J_{BX}|$ and points out the 2-*exo*-position of formyloxy group in **16**. The analogy of chemical shifts of H–C–S protons in **13** (3.27 ppm) and **16** (3.38 ppm) permits us to ascribe the *syn*-configuration of **16**.

DISCUSSION

The main result in principle of this work is the following: The use of formic acid as solvent in addition reactions of DNBSC to olefins leads to the strong increase of the effective electrophilicity of the reagent, shown in (a) occurrance of the Wagner–Meerwein rearrangement and (b) the participation of the solvent in a final step of the addition.

Let us consider some mechanistic aspects of the reaction. Firstly it is known that *p*-chlorobenzenesulphenyl chloride reacts with formic acid to produce the corresponding disulphide and thiolsulphonate.[14] We have shown that DNBSC also reacts with HCOOH to give the dinitrophenyldisulphide. However the rate of this process is evidently less than the rates of the addition reactions.

Secondly it is useful to compare the differences between these addition reactions in acetic vs formic acids. In general the difference has to be due to electrostatic forces in the CH_3COOH on the long distances due to the small dielectric constant of this medium ($\epsilon_{20^\circ}=6.17$). Hence, the ions, if they form, have to join into the ion-pairs (or into the more complex aggregates). Indeed the majority of salts exist in acetic acid as ion-pairs. Therefore the salt effects depending upon the ion-pair interaction are strongly pronounced in this solvent. Hence the success of the earlier proposed method of the increasing of the effective electrophilicity due to the addition of perchlorate salts.[2,3,9]

Formic acid has the large dielectric constant ($\epsilon_{20^\circ}=57.9$) and possesses a larger "ionizing power" than acetic acid.[12] For example the parameters Y, based on tert-butyl chloride solvolysis, are −1.64 (CH_3COOH) and 3.04 (HCOOH) and parameter Y_{2AdOTs}, based on the solvolysis of 2-adamantane derivatives, are −0.61 (CH_3COOH) and 2.05 (HCOOH).[12] Further, tosylate solvolyses (both S_N1 and S_N2) are sharply accelerated in formic acid as compared with acetic acid.[12,18] Different explanations could be advanced for this phenomenon;[12] in particularly the high rate of S_N2 solvolysis in HCOOH is explained with acidic catalysis by hydrogen bonds. It is worth pointing out that formic acid has a large constant of autoprotolysis (1 gK = −6.2) which makes possible both electrophilic and nucleophilic catalysis.

Therefore it is reasonable to suppose that intermediates of type **2** or **3** which are formed at the first step of the addition can rapidly dissociate in HCOOH producing the episulphonium ion in second fast step of the reaction. Another assumption that initial electrophilic reagent, DNBSC, can dissociate in the first rate-determining step in HCOOH, and thus the reaction mechanism is changed to Ad_E1 from usual Ad_E2 one, is less probable. Unfortunately the addition in HCOOH is too fast to be measured by the usual titrimetric procedure.

In conclusion we want to emphasize that independently from the mechanictic details the application of HCOOH as the solvent in the addition reactions of sulphenyl halides (and probably others weak electrophiles) can be regarded as a method for increasing the effective electrophilicity of reagents.

EXPERIMENTAL

Formic acid was purified according to Ref. 14. Dimethoxybenzonorbornadiene **5** was prepared according to Ref. 19. The isolation and purification of the products was done by chromatography on the plates 18 × 24 with silica gel (λ 5/40 and 40/100 μ). Reproducible yields of formates were obtained if the whole work-up was accomplished in one day without delay; otherwise the yield of formates can sharply decrease together with the increasing of the yield of oxy-compounds.

Addition of DNBSC to norbornene **4**

(a) A soln of **4**(0.5 g) and DNBSC (1.15 g) in 10 ml HCOOH was stirred for 20 min at 20°, poured in 50 ml water, extracted with $CHCl_3$. The extracts were washed by water, dried over $MgSO_4$, the solvent was removed and the residue was chromatographed (silica gel λ 5/40, hexane:benzene:ethyl acetate 5:5:2) to give (i) a mixture of **6** and **7** (R_f 0.7 and 0.66) (0.1 g, 7%); (ii) 0.2 g (14%) of **14** (R_f 0.40, m.p. 118.5–119° from CCl_4; found: C, 49.72; H, 3.98. $C_{14}H_{14}N_2O_6S$ requires: C, 49.70; H, 4.17) (PMR spectrum, δ, in CHCl: 3.6, s, 1H, H–C–S; 4.88, q, 1H, H–C–O; IR spectrum: intensive band at 1725 cm^{-1}) and (iv) 0.1 g (34%) of **13** (R_f 0.33, m.p. 140–140.5° from CCl_4–$CHCl_3$, 4:1; found: C, 49.52; H, 4.09; $C_{14}H_{14}N_2O_6S$ requires: C, 49.70; H, 4.17) (PMR spectrum, δ, $CHCl_3$: 3.27, s. 1H, H–C–S; 4.72, t, 1H, H–C–O; IR spectrum: intensive band at 1725 cm^{-1}) and (iv) 0.1 g of unidentified compound, m.p. 260°.

(b) A soln of **4**(0.5 g), DNBSC (1.15 g) and $LiClO_4$ (0.2 g) in 15 ml of HCOOH was stirred for 20 min and the analogous work up gave: (i) 0.6 g (35%) of **13**; (ii) 0.35 g (21%) of **14** and (iii) 0.1 g (6%) of **15** (R_f 0.25, m.p. 152–152.5° from ethanol–hexane, 5:1; found: C, 50.40; H, 4.78. $C_{13}H_{14}N_2O_5S$ requires: C, 50.32; H, 4.55).

Addition of DNBSC to **5**

(a) A soln of **5**(0.5 g) and DNBSC (0.6 g) in 10 ml of HCOOH was stirred for 10 min at 20° and the usual work up including the chromatography on silica gel (λ 40/100 μ, from $CHCl_3$) gave (i) 0.3 g (27%) of **11** (R_f 0.12, m.p. 188–189° from ethanol-ethyl acetate 2:1; lit.[16] m.p. 184°) (PMR spectrum, δ, in $CHCl_3$: AB part of ABX at 1.9–2.75 ppm with J_{AX} 3.6 Hz, J_{BX} 8.2 Hz and J_{AB} 13.9 Hz) and (ii) 0.75 g (67%) of **16** (R_f 0.05, m.p. 168–169° from CCl_4; found: C, 53.69; H, 4.18; S, 7.11. $C_{20}H_{18}N_2O_8S$ requires: C, 53.81; H, 4.06; S, 7.15) (PMR spectrum, δ, in $CHCl_3$: 4.25, q, 1H, H–C–O; 3.38, s, 1H, H–C–S; 3.25 s. 8H, $2OCH_3$, H_1H_4; IR spectrum: intensive band at 1725 cm^{-1}).

(b) A soln of **5** (0.5 g), DNBSC (0.6 g) and $LiClO_4$ (0.12 g) in 10 ml of HCOOH was stirred for 10 min at 20° and the analogous work up gave: (i) 0.3 g (27%) of **11** and 0.6 g (54%) of **16**.

Hydrolysis and acetylation of **13** *and* **14**

(b) A soln of **13** (0.25 g) in 15 ml of 2-n NaOH was refluxed for 30 min, cooled, neutralized by AcOH, extracted with $CHCl_3$ and dried over $MgSO_4$. The chromatography (silica gel, λ 40/100, hexane-benzene-ethyl acetate, 5:5:2) gave 0.16 g (70%) of **15**.

(b) Analogously 0.04 g (44%) of **17** (m.p. 144.5–145° from CCl_4–$CHCl_3$, 1:3) has been obtained from **14** (0.1 g) in 10 ml 2-n NaOH (together with 0.02 g of unchanged **14**).

(c) A soln of **15** (0.15 g) in 1.5 ml of Ac_2O and 1 drop of H_2SO_4 was refluxed for 2 min, poured into water, extracted with $CHCl_3$ and dried over $MgSO_4$. The work up gave 0.1 g of **9** with m.p. 128–129°; lit.[3]: m.p. 129–130°.

(d) Analogously acetylation of **17** (0.04 g) gave the acetate **18** (0.035 g, 79%) with m.p. 125–126°; lit.[3]: m.p. 126–127°.

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