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### Absence of a Special Salt Effect in the Addition of 2,4-Dinitrobenzenesulfonyl Chloride to Norbornene<sup>1</sup>

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The addition of arene and alkanesulfonyl chlorides to alkenes is known to occur in an anti stereospecific manner<sup>2,3</sup> and usually does not involve skeletal rearrangement or formation of large amounts of solvent-incorporated products. A major exception is the report that added LiClO<sub>4</sub> forms substantial amounts of both rearranged and solvent-incorporated products in the addition of 2,4-dinitrobenzenesulfonyl chloride to norbornene in acetic acid.<sup>4</sup> This effect of added salt has been attributed to the same type of special salt effect observed in solvolysis reactions.<sup>4</sup> However, the special salt effect is kinetic in nature<sup>5</sup> while added LiClO<sub>4</sub> is reported to affect only the product composition. To determine if added LiClO<sub>4</sub> also affects the rate as well as the products, we have measured the rate of addition of 2,4-dinitrobenzenesulfonyl chloride to norbornene in acetic acid at various concentrations of LiClO<sub>4</sub>.

### Results and Discussion

The rates of addition of 2,4-dinitrobenzenesulfonyl chloride to norbornene were measured in acetic acid at 25 °C in the presence and absence of added LiClO<sub>4</sub> by a titrimetric method.<sup>6</sup> The additions were found to exhibit normal second-order kinetics, first order in both alkene and sulfonyl chloride to 80% completion of the reaction. The rate data are presented in Table I.

The addition of low concentrations (10<sup>-5</sup>–10<sup>-3</sup>M) of LiClO<sub>4</sub> in acetic acid has no effect upon the rate of addition. This is the concentration range where LiClO<sub>4</sub> causes a special salt effect in solvolysis reactions.<sup>5</sup> As the LiClO<sub>4</sub> concentration is further increased, the rate begins to increase. At a LiClO<sub>4</sub> concentration of 0.536 M, the reaction occurs too fast for accurate determination of the rate constant by our technique. However, the rate increases caused by LiClO<sub>4</sub> concentrations of 0.0815 and 0.536M are about that expected from the work of Kharasch.<sup>6</sup>

Table I. Second-Order Rate Constants for the Addition of 2,4-Dinitrobenzenesulfonyl Chloride to Norbornene in Acetic Acid at 25 °C in the Presence of Varying Amounts of LiClO<sub>4</sub>

10 <sup>-3</sup> [norbornene], M	10 <sup>-3</sup> × [ArSOCl], M	[LiClO <sub>4</sub> ], M	k, M <sup>-1</sup> s <sup>-1</sup>
5.38	4.02	0	0.107 ± 0.007
5.96	7.94	0	0.10 ± 0.01
5.38	8.06	0	0.0980 ± 0.008
8.98	6.92	0	0.114 ± 0.008
8.98	6.92	4.29 × 10 <sup>-5</sup>	0.113 ± 0.005
5.96	7.94	5.64 × 10 <sup>-5</sup>	0.103 ± 0.008
6.68	7.94	1.13 × 10 <sup>-4</sup>	0.10 ± 0.01
8.00	6.92	4.29 × 10 <sup>-4</sup>	0.10 ± 0.01
8.00	6.92	8.58 × 10 <sup>-4</sup>	0.100 ± 0.008
8.98	6.92	8.58 × 10 <sup>-4</sup>	0.103 ± 0.008
8.00	6.92	4.29 × 10 <sup>-3</sup>	0.092 ± 0.005
8.98	6.92	4.29 × 10 <sup>-3</sup>	0.101 ± 0.008
8.98	6.92	8.15 × 10 <sup>-2</sup>	0.126 ± 0.003
6.27	7.94	5.36 × 10 <sup>-1</sup>	0.5 ± 0.1

The first conclusion reached from the data in Table I is that the effect of added LiClO<sub>4</sub> is not a special salt effect. The lack of such an effect indicates that added LiClO<sub>4</sub> does not increase the electrophilicity of the arenesulfonyl chloride in this addition reaction as claimed by Zefirov.<sup>4</sup> From the data in Table I, further conclusions can be reached about specific details of the mechanism of arenesulfonyl chloride additions to alkenes.

The two-step mechanism originally proposed by Kharasch<sup>7</sup> has been expanded to include a number of ion-pair intermediates as shown in the Scheme I.<sup>3</sup> The existence of ion-pair intermediates in electrophilic additions has been proposed by a number of investigators.<sup>8-11</sup>

Structures 1 and 2 are intimate ion pairs while 3 and 4 are solvent-separated ion pairs.<sup>12</sup> The difference between 1 and 3 and 2 and 4 is the location of the counterion. In 1 and 3, the chloride ion is near sulfur while in 2 and 4, the chloride ion is near carbon. The pathway involving ions 2, 4, and 5 is the general solvolysis scheme proposed by Winstein.<sup>5</sup> The solvolysis of β-chloroalkyl aryl sulfides meets the requirements for solvolysis by means of any or all of the ions 2, 4, and 5.<sup>13</sup> The pathway involving ions 1, 3, and 5 is based on a similar scheme proposed for the chlorination of alkenes.<sup>14</sup> The experimental data that

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(4) (a) Zefirov, N. S.; Sadorvaya, N. K.; Magerramov, A. M.; Bodrikov, I. V.; Kartashov, V. R. *Tetrahedron* 1975, 31, 2948. (b) Zefirov, N. S.; Sadorvaya, N. K.; Novgorodtseva, L. A.; Akhmedova, R. S.; Bodrikov, I. V. *Ibid.* 1979, 35, 2759.

(5) Winstein, S.; Morse, B. K. *J. Am. Chem. Soc.* 1952, 74, 1133. Winstein, S.; Trefan, D. *Ibid.* 1952, 74, 1154. Winstein, S.; Schreiber, K. C. *Ibid.* 1952, 74, 2165. Fainberg, A. H.; Winstein, S. *Ibid.* 1956, 78, 2763. Winstein, S.; Friedrich, E. C.; Smith, S. *Ibid.* 1971, 93, 5705.

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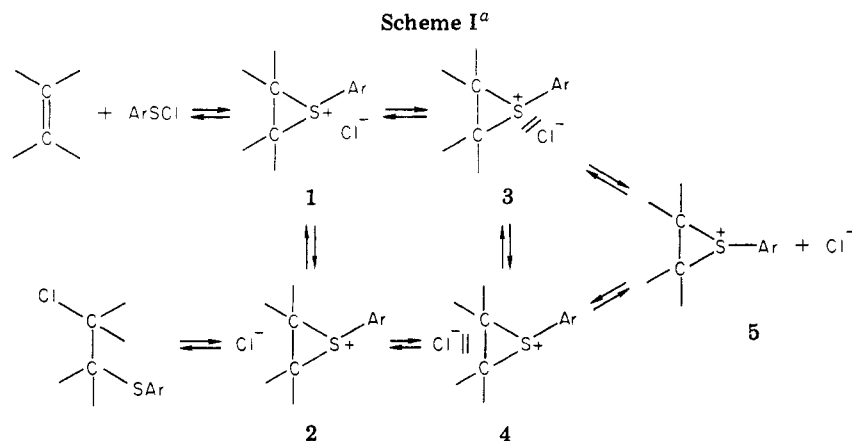
(10) Fahey, R. S. *Top. Stereochem.* 1968, 3, 237. De la Mare, P. B. D.; Bolton, R. "Electrophilic Additions to Unsaturated Systems"; Elsevier: Amsterdam, 1966.

(11) Zefirov, N. S.; Koz'min, A. S.; Kirin, V. N.; Zhdankin, V. V.; Caple, R. *J. Org. Chem.* 1981, 46, 5264.

(12) To avoid confusion, we have adopted the original Winstein<sup>5</sup> definition of intimate and solvent-separated ion pairs.

(13) Fitzgerald, P. H. Ph.D. Thesis, University of Toronto, 1972.

(14) Poutsma, M. L. *Science* 1967, 157, 997. Cabaleiro, M. C.; Johnson, M. D. *J. Chem. Soc. B* 1967, 565.



<sup>a</sup> Ar = arene.

requires a connection between these two pathways has been summarized in ref 3.

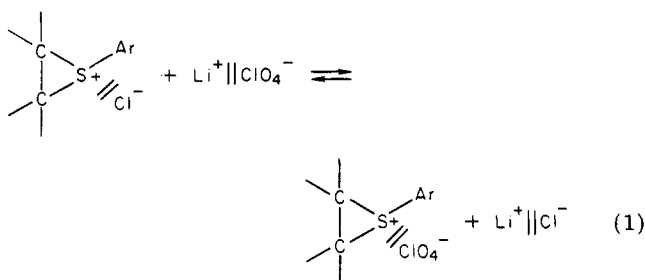
The special salt effect is believed to cause a rate increase by preventing the return to starting material of solvent-separated ion pairs.<sup>15</sup> Instead, the solvent-separated ion pairs are diverted to product. The absence of any special salt effect on the rate of addition is evidence that the reactions of the solvent-separated ion pair 3 are not the rate-determining steps. Thus the rate-determining step must occur before the reactions of 3. This is in accord with the suggestion made several years ago that in the additions of arenesulfonyl chlorides to alkenes the double bond acts as a nucleophile and that its attack at sulfur is rate determining.<sup>16</sup>

This view is supported by two reactions of arenesulfonyl chlorides in which special salt effects have been observed. Kwart et al. found that the chlorination of 4-substituted benzenesulfonyl chlorides to sulfonyl chlorides in acetic acid exhibits a strong special salt effect.<sup>17</sup> A Hammett  $\rho$  value of -2.44 was obtained. A mechanism was proposed involving rate-determining substitution on tetravalent sulfur by a hydroxylic component of the medium in an  $S_N1$ -type process involving ion-pair intermediates.

Ciuffarin found that added  $\text{LiClO}_4$  exerts a strong accelerating effect upon the reaction of 4-nitrobenzenesulfonyl chloride and aniline in benzene.<sup>18</sup> Kinetic analysis of their data lead to the conclusion that an intermediate is formed and that its reaction to products is rate determining.

The important point of these studies is that evidence is presented for rate-determining reaction of a tetravalent sulfur intermediate or intimate ion pair. Both reactions show strong special salt effects, and the Hammett  $\rho$  value of one reaction indicates a relatively strong substituent effect. In contrast, no special salt effect is found in our work, and substituent effects at sulfur are known to be small<sup>19</sup> and/or variable.<sup>20</sup> Such a comparison supports the view that the mechanism of arene- and alkanesulfonyl chloride additions to alkenes in acetic acid involves synchronous, direct displacement at sulfur similar to the  $S_N2$  mechanism at  $sp^3$  carbon.

The effect of added  $\text{LiClO}_4$  on the product composition may be due to a specific exchange of chloride ion by perchlorate ion in the solvent-separated ion pairs<sup>21</sup> (eq 1).



This is identical with the effect of  $\text{LiClO}_4$  in the special salt effect.<sup>21</sup> However, since it occurs after the rate-determining step, it does not affect the rate. The thiiranium perchlorate solvent-separated ion pair would lead to solvent-incorporated or rearranged products rather than the normal  $\beta$ -chlorosulfide adduct. On the other hand, the high concentrations of  $\text{LiClO}_4$  used in the product studies ( $\sim 1.0$  M) may simply change the ionizing power of the medium. Such an effect, often caused by added electrolytes, would increase the concentration of ion-pair 3 and ion 5 with a consequent increase in rearranged and solvent-incorporated products.<sup>22</sup>

In summary, the presence of added  $\text{LiClO}_4$  does not increase the electrophilicity of 2,4-dinitrobenzenesulfonyl chloride in its addition reactions to norbornene in acetic acid despite claims to the contrary. Comparison of our results with data in the literature supports the view that the structure of the rate-determining transition state in this reaction is similar to that in the  $S_N2$  mechanism at  $sp^3$  carbon. The difference in the effect of added  $\text{LiClO}_4$  on the rate and the product composition clearly indicates that there is more than one intermediate involved in this addition reaction.

### Experimental Section

All boiling and melting points are uncorrected.

**Materials.** Acetic acid was purified by modifying the method of Kendall and Cross.<sup>23</sup> Concentrated  $\text{H}_2\text{SO}_4$  (2 mL/2.5 L of acetic acid) was used as a catalyst: bp 116 °C; fp/16.60 °C. The distilled acetic acid contained  $0.004 \pm 0.001\%$  water as determined by Karl Fischer titration.

(15) Winstein, S.; Clippinger, E.; Fainberg, A. H.; Robinson, G. C. *J. Am. Chem. Soc.* 1954, 76, 2597. Winstein, S.; Klinedinst, P. E., Jr.; Robinson, G. C. *Ibid.* 1961, 83, 885.

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(17) Givens, E. N.; Kwart, H. *J. Am. Chem. Soc.* 1968, 90, 378, 386.

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**Anhydrous LiClO<sub>4</sub>** was obtained from Alfa Products. It was dried in a drying pistol at 100 °C (0.38mmHg) in the presence of P<sub>2</sub>O<sub>5</sub> for at least 12 h.

**Norbornene** was obtained from Aldrich Chemical Co. and used without further purification. No impurities were detected by GLC analysis on a 3% OV-101 column with CHRM GHP as the support (80/100 mesh) at 80 °C with N<sub>2</sub> as a carrier gas and an FID detector.

**2,4-Dinitrobenzenesulfonyl chloride (2,4-DNBSCl)** was obtained from Aldrich Chemical Co. and recrystallized from CCl<sub>4</sub>; mp 95.6-96.6 °C (lit.<sup>24</sup> mp 95-96 °C)

**Kinetics.** Separate solutions of 2,4-DNBSCl in acetic acid and a mixture of norbornene and LiClO<sub>4</sub> in acetic acid were equilibrated in an oil bath at 25.00 ± 0.05 °C. After the solutions were mixed, aliquots were withdrawn periodically, and the remaining 2,4-DNBSCl was analyzed by the method of Kharasch and Wald.<sup>25</sup>

**Acknowledgment.** Continued financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

**Registry No.** 2,4-DNBSCl, 528-76-7; LiClO<sub>4</sub>, 7791-03-9; norbornene, 498-66-8.

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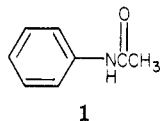
### Directing Effects of Phosphorus-Containing Groups in Aromatic Substitution. Orientation in Nitration of Some *N*-Arylphosphoramidates and Phosphorothioamidates in Protic and Aprotic Media

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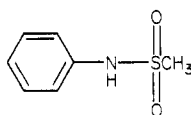
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The nitration of acetanilide **1** in strong acid is known<sup>1,2</sup> to give predominantly para product with some ortho substitution and negligible meta product (Table I).



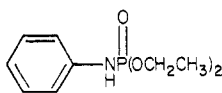
1

Under identical conditions,<sup>1</sup> the corresponding sulfur compound **2** gives a 70:30 para/ortho nitration product distribution (Table I).



2

Published results for the related phosphorus derivative **3** are substantially different, with a considerable amount



3

of meta product being formed (Table I).<sup>3</sup> The meta

(1) Hartshorn, S. R.; Moodie, R. B.; Schofield, K. *J. Chem. B* 1971, 2454.

(2) Haggett, J. C.; Moodie, R. B.; Penton, J. R.; Schofield, K. "Nitration and Aromatic Reactivity"; Cambridge University Press: London, 1971; Chapter 5, Section 3.4.

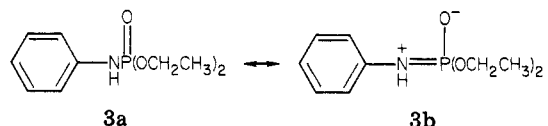
(3) Modro, T. A.; Pioch, J. *Can. J. Chem.* 1976, 54, 560.

Table I. Isomers from Nitration in Protic Media

compd	conditions	distribution, %		
		ortho	meta	para
1 <sup>1,2</sup>	HNO <sub>3</sub> -98% H <sub>2</sub> SO <sub>4</sub> , 25 °C	5	< 2	95
2 <sup>1</sup>	HNO <sub>3</sub> -98% H <sub>2</sub> SO <sub>4</sub> , 25 °C	30	< 1	70
3 <sup>3</sup>	HNO <sub>3</sub> -97% H <sub>2</sub> SO <sub>4</sub> , 0 °C	42	38	20
3 <sup>a</sup>	HNO <sub>3</sub> -97% H <sub>2</sub> SO <sub>4</sub> , 0 °C	3	70	27
4	HNO <sub>3</sub> -97% H <sub>2</sub> SO <sub>4</sub> , 0 °C	< 2	72	28
5	HNO <sub>3</sub> -97% H <sub>2</sub> SO <sub>4</sub> , 0 °C	3	79	18
6	HNO <sub>3</sub> -97% H <sub>2</sub> SO <sub>4</sub> , 0 °C	7	< 2	93

<sup>a</sup> Present work.

product for **3** was rationalized in terms of two possible phenomena: (a) nitration via the N-protonated form or (b) a substantial amount of N-P pπ-dπ bonding leading to important contributions from the resonance form **3b**.



3a

3b

Recently we have carried out <sup>15</sup>N and <sup>13</sup>C NMR studies of **3** and related phosphoramidates<sup>4,5</sup> which show that there is negligible contribution from resonance forms such as **3b**, since N lone-pair delocalization into the aromatic ring is found to be the dominant process.

One is led therefore to the conclusion that systems such as **3** nitrate to a significant extent via the N-protonated form in acidic media. In aprotic media, one might expect to see, however, a return to mainly ortho-para product distribution.

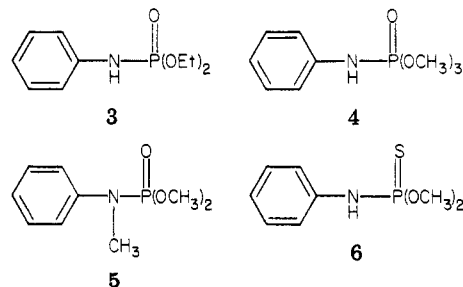
To check this point, we have carried out the nitration of **3** in an aprotic medium, namely, via the pyridine-nitronium tetrafluoroborate complex.<sup>6</sup>

Also we have repeated the protic media nitration of **3** and related compounds in order to verify the reported<sup>3</sup> high degree of ortho products. No yields of isolated and separated products were quoted<sup>3</sup> in previous work, and isomer ratios were given to a ±10% accuracy by using a TLC-spectrophotometric procedure.<sup>7</sup>

In the present work, we have isolated and characterized the nitration products (in the form of their nitroaniline derivatives) and compared them to commercially available standards in order to obtain more reliable data regarding the nitration product distribution.

### Results and Discussion

**Protic Nitrations.** Nitrations in protic media were carried out for compounds **3-6**, and results are summarized in Table I along with those reported previously.



5

6

Each value in the present work represents an average of at least four determinations with standard deviations

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(5) Buchanan, G. W.; Morin, F. G. *Org. Magn. Reson.* 1980, 14, 517.

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