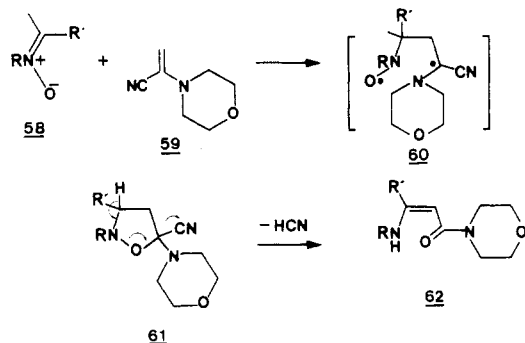
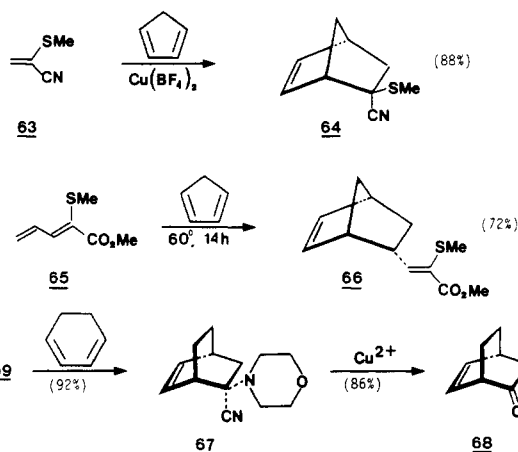


pecific (3 + 2) cycloaddition to  $\alpha$ -morpholinoacrylonitrile (59) whereby the stabilized biradical 60 may be the intermediate. The oxazolidines 61 cannot be isolated, as they undergo an eliminative ring-opening to push-pull amides 62.<sup>50</sup> The versatile  $\alpha$ -(tert-butylthio)acrylonitrile (52) can even act as the  $\pi$ -4 component in (3 + 2) cycloadditions with electron-poor dienophiles, e.g., *N*-phenylmaleic imide, maleic anhydride, and acetylenedicarboxylate.<sup>51</sup>



Finally, captodative olefins and dienes react cleanly as  $\pi$ -2 components in Diels-Alder reactions.<sup>52</sup> The  $\alpha$ -(methylthio)acrylonitrile (63) exhibits more dienophilic character than acrylonitrile or  $\alpha$ -chloroacrylonitrile.<sup>52c</sup> The captodative dienes, e.g., 65, react at the less substituted double bond with unactivated dienes.<sup>52c</sup> The cycloadducts (e.g., 67) of  $\alpha$ -morpholinoacrylonitrile (59) are easily transformed to the corresponding ketones 68. Thus, this captodative olefin constitutes a new ketene equivalent.<sup>52b</sup> Owing to the numerous possi-



bilities offered by variations of the captodative substitution and by their further transformations, the new concept provides a general approach for organic synthesis of polyfunctional compounds via radicals, especially in the field of selective reduction and oxidation, substitution, addition, and cycloaddition reactions.

### Outlook

Although much work still remains to be done, the captodative substituent effect now emerges as theoretically and experimentally well-founded. The captodative concept has proven to be useful in explaining many phenomena and in stimulating synthetic work. The applications are anticipated to reach beyond chemistry to all fields where unpaired electrons are occurring, last but not least in life processes.

*We gratefully acknowledge the valuable contribution of numerous co-workers whose names appear on the articles quoted in this Account. We are particularly indebted to Professors H. G. Aurich, Sir Derek Barton, R. Louw, G. Leroy, R. Sustmann, and Lord Tedder for valuable discussions. Acknowledgment is also made to SPPS Grant 79/84-13 for financial support of this research.*

- (49) Alder, A.; Belluš, D. *J. Am. Chem. Soc.* **1983**, *105*, 6712.  
 (50) Döpp, D.; Walter, J. *Heterocycles* **1983**, *20*, 1055.  
 (51) Döpp, D.; Libera, H. *Tetrahedron Lett.* **1983**, *24*, 885.  
 (52) (a) Stella, L.; Boucher, J. L. *Tetrahedron Lett.* **1982**, *23*, 953. (b) Boucher, J. L.; Stella, L. *Tetrahedron*, in press. (c) Boucher, J. L. Ph. D. work, Marseille 1984.

## Competitive Binding of Nucleofugal Anions in Carbocationic-like Processes

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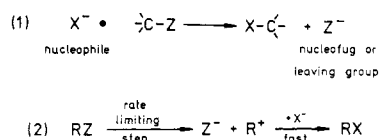
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The concept of *nucleophilicity* has been a cornerstone of organic chemistry ever since the early investigations of Ingold and co-workers.<sup>1</sup> The definition of *nucleophilic reactions* forms an important conceptual

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basis. For many years they were the favorites of physical organic chemists. In his classical work Ingold clearly defined a series of reaction mechanisms with two limiting cases of  $S_N2$  (eq 1) and  $S_N1$  (eq 2) type.



Equation 1 clearly demonstrates that nucleophiles and nucleofuges are basically species of the same sort.

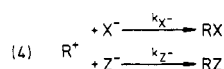
(1) C. K. Ingold "Structure and Mechanism in Organic Chemistry", 2nd ed., Cornell University Press, Ithaca, N.Y., 1969, Chapter 7.

However, there is no simple (e.g., inverse) correlation between the nucleophilic and nucleofugal properties of anions. A quantitative statement of nucleophilicity, which is a kinetic property is often based on its rate constant for the  $S_N2$  reaction, in terms of the Swain-Scott scale.<sup>2</sup> Data about nucleofugality can be extracted either from  $S_N2$  reactions<sup>3</sup> or from elimination ones.<sup>4</sup>

The  $S_N1$  process includes the fast interaction of a carbocation and a nucleophile in a simple combination reaction (eq 3). The usual way to study anionic nu-



cleophilicity of such processes involves competitive reactions (eq 4) and the determination of selectivities,  $S = k_X/k_Z = [RX][Z^-]/[RZ][X^-]$ .<sup>5,6</sup> Pioneering work by Ritchie<sup>7,8</sup> revealed a spectacular constancy of selectivities of stable cations of widely varying reactivities toward nucleophiles. In other words, the rate constant ratio (eq 4) often remains constant until limiting values due to desolvation of diffusion are reached.<sup>7-9</sup>

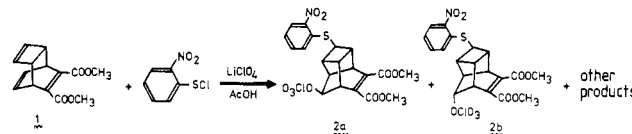


For present purposes one silent point may be emphasized: all the suggested scales of nucleophilicity or nucleophilic orders<sup>2,10</sup> completely ignore the nucleophilic properties of certain "supernucleofugal" anions, such as  $ClO_4^-$ ,  $FSO_3^-$ , and  $CF_3SO_3^-$  and, moreover, even of such a typical nucleofuge as the *p*-toluenesulfonate ion. Generally these anions are considered as inert additives in competitive processes of the type shown in eq 4,<sup>12</sup> unable to interfere in the reaction by competitive trapping of carbocationic intermediates. Hence, the main application of the salts containing super-nucleofugal anions (e.g.,  $LiClO_4$ ) has been in the maintaining of constant ionic strength, in the study of salt effects, as a supporting electrolyte in electrochemistry, etc. While rare kinetic data have been interpreted in terms of carbenium perchlorate ion pair return to covalent perchlorate,<sup>14</sup> the possibility of covalent perchlorate formation by capturing carbocationic-like intermediates in the presence of other anionic nucleophiles or nucleophilic solvents is usually ignored.

In 1978 we serendipitously found (in the course of

- (2) C. G. Swain and C. C. Scott, *J. Am. Chem. Soc.* **75**, 141 (1953).
- (3) D. N. Kevill and G. M. Lin, *Tetrahedron Lett.* 949 (1978).
- (4) B. Issari and C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 2* 1043 (1984); C. J. M. Stirling, *Acc. Chem. Res.*, **12**, 198 (1979).
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- (6) D. J. McLennan, *Acc. Chem. Res.*, **9**, 281 (1976) and references therein.
- (7) C. D. Ritchie and P. O. I. Virtanene, *J. Am. Chem. Soc.*, **95**, 1882 (1972); **94**, 4963, 4966 (1972).
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- (9) (a) J. P. Richard and W. P. Jenks, *J. Am. Chem. Soc.*, **106**, 1373, 1383, 1396 (1984); (b) J. P. Richard, M. E. Rothenberg, and W. P. Jenks, *ibid.* **106**, 1361 (1984).
- (10) "Chemical Reactivity and Reaction Paths", G. Klopman, Ed., Wiley, New York, 1973, Chapters 4 and 5.
- (11) There are many papers where these ions were labeled as "nonnucleophilic" or, shyly, "essentially nonnucleophilic" ones.
- (12) Carbocations can react with "nucleofugal" anions in the absence of other nucleophilic reagents to give covalent products in accordance with eq 3, at least in media of low polarity and acidity. The most useful way by utilization, under heterogeneous conditions, of silver salts with "nucleofugal" counteranions. A promising new method is the application of "betylates".<sup>13</sup>
- (13) J. F. King, S. M. Loosmore, M. Aslam, and M. J. McGarrity, *J. Am. Chem. Soc.*, **104**, 7108 (1982) and references therein.
- (14) A. Ehert and S. Winstein, *J. Am. Chem. Soc.* **88**, 2048 (1966); Y. Pocker and B. P. Ronald, *ibid.* **102**, 5311 (1980).

our investigation of "doping-addition"<sup>15,16</sup>) an astonishing phenomenon: the addition of (2-nitrophenyl)sulfonyl chloride to diester **1** in acetic acid in the presence of  $LiClO_4$  gave the perchlorates **2** (16% yield) together with other products.<sup>16-18</sup> This fact is amazing:

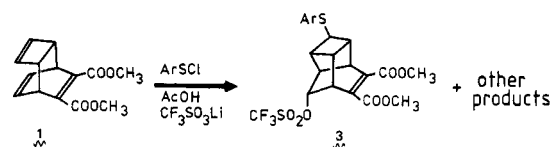


$ClO_4^-$  plays the role of a nucleophile which can successfully compete with the chloride ion and even with the solvent, AcOH ( $S_{LiClO_4}/AcOH \approx 9!$ ), in attack on the carbocationic center in the final step of the addition.

Extention of this work has shown that the competitive covalent binding of "nucleofugal" anions (including  $CF_3SO_3^-$ ,  $ClO_4^-$ , and  $FSO_3^-$ ) is a general phenomenon for a variety of carbocationic-like reactions, including electrophilic additions,<sup>16-20</sup> deamination of amines,<sup>20,21</sup> acid-catalyzed epoxide ring opening,<sup>20,22,23</sup> and deiodination of alkyl iodides.<sup>20,24</sup>

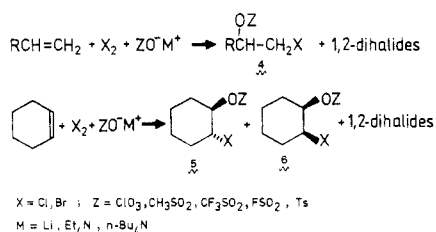
### General and Synthetic Aspects

Electrophilic additions to C=C double bond proceeding via transient formation of carbocationic-like intermediates have been studied in detail. The initially observed reaction,  $1 \rightarrow 2$ , was echoed in the analogous addition of other sulfonyl chlorides<sup>16,17</sup> and phenylselenyl chloride<sup>25</sup> to diester **1** and related dienes.<sup>16,26</sup> The analogous reaction in the presence of  $CF_3SO_3Li$  proceeds to give the triflate **3**.<sup>27</sup> While the yield of **3** is only 12%, this result is especially remarkable in view of the very highly nucleofugal property of the trifluoromethanesulfonate anion, even in comparison with  $ClO_4^-$ .<sup>3</sup>

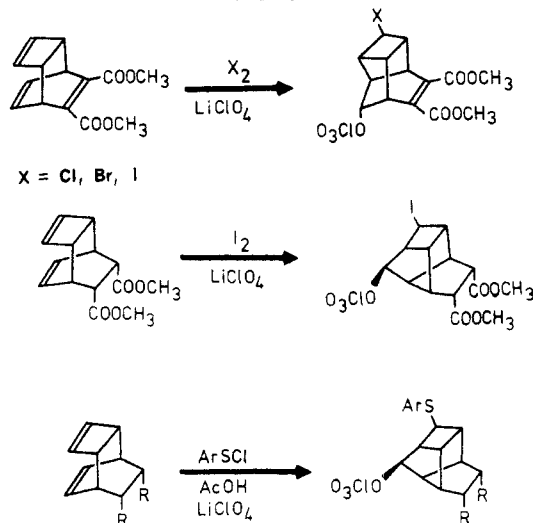


- (15) (a) N. S. Zefirov, N. K. Sadovaja, L. A. Novgorodtseva, R. Sh. Akhmedova, S. V. Baranov, and I. V. Bodrikov, *Tetrahedron*, **35**, 2759 (1979). (b) W. A. Smit, N. S. Zefirov, I. V. Bodrikov, and M. Z. Krimer, *Acc. Chem. Res.*, **12**, 282 (1979).
- (16) N. S. Zefirov, A. S. Kozmin, V. N. Kirin, V. V. Zhdankin, and R. Caple, *J. Org. Chem.*, **46**, 5264 (1981) and references therein.
- (17) N. S. Zefirov, A. S. Kozmin, V. N. Kirin, V. V. Zhdankin, and I. V. Bodrikov, *Zh. Org. Khim.*, **14**, 2615 (1978).
- (18) N. S. Zefirov, A. S. Kozmin, V. V. Zhdankin, A. V. Nikulin, and N. V. Zyk, *J. Org. Chem.*, **47**, 3679 (1982).
- (19) N. S. Zefirov, A. S. Kozmin, and V. V. Zhdankin, *Tetrahedron*, **38**, 291 (1982).
- (20) N. S. Zefirov, A. S. Kozmin, V. V. Zhdankin, V. N. Kirin, N. M. Yur'eva, and V. D. Sorokin, *Chem. Scr.* **22**, 195 (1983).
- (21) N. S. Zefirov, A. S. Kozmin, V. N. Kirin, N. M. Yur'eva, and V. V. Zhdankin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2634 (1982).
- (22) N. S. Zefirov, A. S. Kozmin, N. M. Yur'eva, V. V. Zhdankin, and V. N. Kirin, *Zh. Org. Khim.* **18**, 2211 (1982); D. S. Yufit, Yu. T. Struchkov, N. M. Yur'eva, A. S. Kozmin, and N. S. Zefirov, *Cryst. Struct. Commun.* **11**, 1903, (1982).
- (23) N. S. Zefirov, A. S. Kozmin, N. M. Yur'eva, V. V. Zhdankin, and V. N. Kirin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 707 (1983).
- (24) (a) N. S. Zefirov, V. V. Zhdankin, and A. S. Kozmin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1676 (1982). (b) N. S. Zefirov, A. S. Kozmin, V. V. Zhdankin, V. D. Sorokin, Yu. V. Dankov, and V. N. Kirin, *Zh. Org. Khim.* **18**, 2617 (1982). (c) N. S. Zefirov, V. V. Zhdankin, and A. S. Kozmin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1682 (1983).
- (25) D. G. Garratt, M. D. Ryan, and A. Kabo, *Can. J. Chem.*, **58**, 2329 (1980).
- (26) N. S. Zefirov, V. N. Kirin, A. S. Kozmin, I. V. Bodrikov, K. A. Potekhin, and E. N. Kurkutova, *Tetrahedron Lett.*, 1547 (1979).
- (27) N. S. Zefirov, A. S. Kozmin, V. D. Sorokin, and V. V. Zhdankin, *Zh. Org. Khim.*, **19**, 876 (1983).

## Scheme I



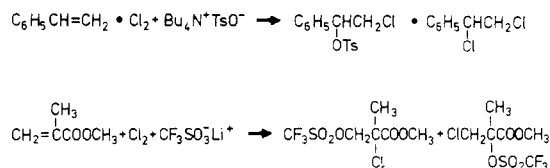
## Scheme II



However, *preparative* yields of the target derivatives of "nucleofugal" anions have been achieved in nonnucleophilic solvents. We have studied the involvement of a variety of "nucleofugal" anions during the addition of several electrophiles, including  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{ArS-Cl}$ , and  $\text{PhI(OH)OTs}$  (where OTs stands for *p*-toluenesulfonate) to olefins in many aprotic solvents.<sup>18,19,28,29</sup> In many cases we have been able to isolate, purify, and identify the desired esters of perchloric and sulfonic acids; some typical examples are shown in Scheme I.

These reactions proceed very rapidly even at  $-70^\circ\text{C}$  in the presence of 1.5–2 M lithium or tetraalkylammonium salts to give 20–70% yields of the indicated ester adducts. The addition to heptene-1 proceeds in accordance with the Markovnikov rule to give compounds of type 4.<sup>18,28</sup> While trans addition to cyclohexene is usually predominant, we have occasionally obtained the corresponding cis adducts 6 as minor products.<sup>18</sup>

The examples of chlorination of styrene<sup>29</sup> and methyl methacrylate<sup>30</sup> show that covalent derivatives of "nucleofugal" anions can be obtained even at benzylic and tertiary carbon atoms.



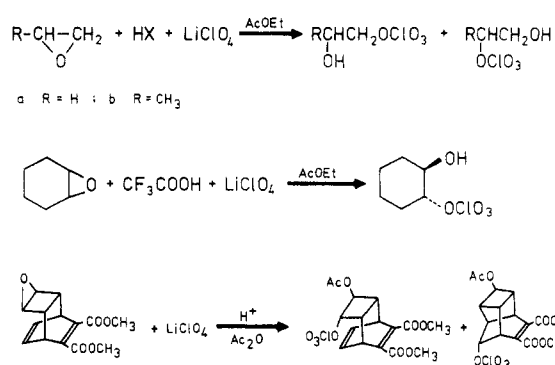
Especially impressive yields of the cage derivatives of the tricyclo[4.2.0.0<sup>2,5</sup>] decane system have been ob-

(28) (a) N. S. Zefirov, A. S. Kozmin, Yu. V. Dan'kov, V. V. Zhdankin, and V. N. V. N. Kirin, *Zh. Org. Chem.*, **20**, 233 (1984). (b) N. S. Zefirov, A. S. Kozmin, V. D. Sorokin, and V. V. Zhdankin, *ibid.*, **18**, 1768 (1982).

(29) N. S. Zefirov, V. V. Zhdankin, Yu. V. Dan'kov, V. V. Samoshin, and A. S. Kozmin, *Zh. Org. Chem.*, **20**, 444 (1984).

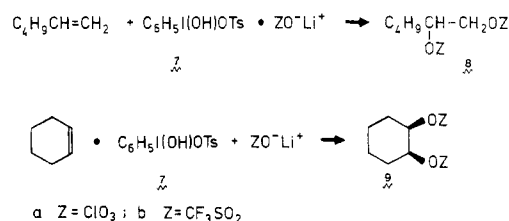
(30) N. S. Zefirov and A. S. Kozmin in "Soviet Scientific Reviews", Vol. 7, M. E. Vol'pin, Ed., Harwood Academic Publishers, New York, in press.

## Scheme III



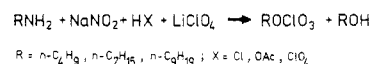
tained due to (i) the predominance of the pathway of capture of the "nucleofugal" anions<sup>16,17,19,27</sup> and (ii) the stability of the corresponding derivatives, which incidentally permitted proof of their structures beyond the shadow of a doubt by X-ray analysis.<sup>31</sup> Further examples of these reactions are shown in Scheme II.

Addition of (hydroxy(tosyloxy)iodo)benzene (7) to olefins produces vic-bis(*p*-toluenesulfonates).<sup>32a</sup> We have found that the addition of reagent 7 in the presence of  $\text{LiClO}_4$  or  $\text{CF}_3\text{SO}_3\text{Li}$  proceeds to give vicinal diesters of perchloric (8a and 9a) and trifluoromethanesulfonic (8b and 9b) acids.<sup>29b</sup> While the yields of these compounds are modest (20–30%), the simplicity of the method is remarkable.<sup>32b</sup>



These examples clearly demonstrate the generality of electrophilic additions to olefins in which the nucleophilic addend is a perchlorate, trifluoromethanesulfonate, or *p*-toluenesulfonate ion. It is probable that other electrophiles as well as other unsaturated compounds (allenes, acetylenes, and even cyclopropanes) may be involved in analogous transformations.

**Deamination of amines** by nitrous acid involves the production of diazonium ions which lose nitrogen to give cationic intermediates. We have studied the reactions of several alkylamines with  $\text{NaNO}_2$  in the presence of acid and specially added  $\text{LiClO}_4$  in different solvents ( $\text{AcOEt}$ ,  $\text{Et}_2\text{O}$ , and even  $\text{H}_2\text{O}$ ) and in every case could identify the formation of alkyl perchlorates; in many cases they were isolated after a rapid workup of the reaction mixtures.<sup>20,21</sup>

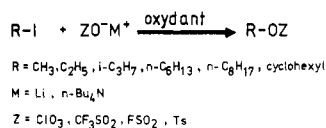


The yields of perchlorates are modest and changeable; nevertheless, these reactions illustrate the generality of the observed phenomenon.

(31) Selected examples of X-ray data are given by: V. I. Bondar and co-workers, *Cryst. Struct. Commun.*, **10**, 587 (1981); T. F. Rau and co-workers, *ibid.*, **11**, 207 (1982); N. S. Zefirov and co-workers, *ibid.*, **11**, 1921 (1982).

(32) (a) L. Rebrovic and G. F. Koser, *J. Org. Chem.*, **49**, 2462 (1984). (b) The best way to obtain 1,2-vic-diperchlorates or -ditriflates is to use specially prepared  $\mu$ -oxodiphenyldiodo derivatives, e.g., perchlorate or triflate ( $\text{PhI(X)O(X)IPh}$ , where X =  $\text{OClO}_3$  or  $\text{OSO}_2\text{CF}_3$ ).<sup>28a,29</sup>

## Scheme IV

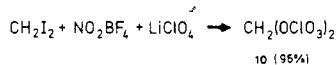


**Acid-catalyzed cleavage of epoxides** is a reaction having considerable S<sub>N</sub>1 character. We have studied the ring opening of epoxides by action of protic acids in the presence of LiClO<sub>4</sub> and observed the formation of the corresponding perchlorates.<sup>21,22</sup> Representative examples are given in Scheme III.

The obtained hydroxyperchlorates are rare examples of bifunctional substances containing reactive electrophilic and nucleophilic centers that do not self-annihilate; hence, they may offer unusual opportunities for synthesis.

**Oxidative deiodination** of alkyl iodides involves carbocationic-like intermediates. We have studied the oxidative deiodination of alkyl iodides with different oxidants in the presence of a salt of perchloric, trifluoromethanesulfonic, fluorosulfonic, or arylsulfonic acid in inert solvents. In all cases the corresponding esters were obtained (20–70%).<sup>24</sup> This process is a very convenient synthetic method (Scheme IV).

It is well-known that BF<sub>4</sub><sup>-</sup> anion can play the role of a nucleophilic species in the final step of some carbocationic-like processes,<sup>33</sup> acting as a source of a fluoride anion. However the “nucleofugal” anions surpass the fluoroborate ion in capturing carbocationic intermediates. In fact, NO<sub>2</sub>BF<sub>4</sub> can play the role of an excellent oxidant in these reactions. Using it, we have been able to synthesize some interesting compounds, such as 10.<sup>20,34</sup>



In conclusion we stress two points. First, the competitive binding of “nucleofugal” anions, which were regarded as super weak nucleophiles, is a general phenomenon.

Second, one of the useful results has been the discovery of a variety of novel reactions leading to compounds with covalent bonds between carbon and groups of high nucleofugality. These procedures can undoubtedly compete with existing synthetic methods, especially in the case of esters of perchloric acid. Moreover, the ability of the derivatives of “nucleofugal” anions to undergo nucleophilic substitution<sup>35</sup> and the possibility of using them without isolation (one-pot synthesis) permit one to expect that future studies will reveal appreciable synthetic potential for these reactions.

### Theoretical Aspects

While our work has had mainly a synthetic trend, it has served to identify some points of theoretical importance. The competitive formation of covalent derivatives of “nucleofugal” anions can be realized only

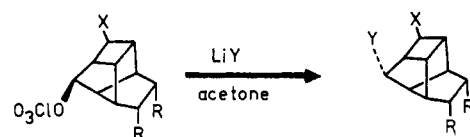
(33) (a) S. A. Chakelford, *J. Org. Chem.*, **44**, 3485 (1979). (b) M. I. Kanishev, A. A. Schegolev, W. A. Smit, R. Caple, and M. J. Kelner, *J. Am. Chem. Soc.*, **101**, 5560 (1979). (c) S. I. Anfilogova, E. B. Frolov, Yu. N. Luzikov, and E. S. Balenkova, *Zh. Org. Khim.*, **15**, 1432 (1979).

(34) Moreover, NO<sub>2</sub>BF<sub>4</sub> + LiClO<sub>4</sub> can be regarded as a good reagent which interacts with olefins to give 1,2-nitroperchlorates<sup>18</sup> and with epoxides to give 1,2-nitroperchlorates.<sup>20,23</sup>

(35) N. S. Zefirov, A. S. Kozmin, and V. V. Zhdankin, *Dokl. Akad. Nauk SSSR*, **262**, 104 (1982).

if (i) S<sub>N</sub>2 reactions of the newly formed derivatives with other nucleophiles are blocked and (ii) the nucleophilicity of “nucleofugal” anions toward carbocationic-like species is sufficiently high to enable them to compete with other nucleophilic species. The previous section clearly demonstrates that both these requirements can be satisfied surprisingly easily.

The first crucial factor, namely, the absence of subsequent S<sub>N</sub>2 reactions, seems to be self-evident. It is well-known that only free chloride ions react in S<sub>N</sub>2 reactions of LiCl in acetone, the ion pair being unreactive.<sup>36</sup> Hence, solvents of low polarity act to suppress S<sub>N</sub>2 reactions of covalent perchlorates with LiCl. Indeed, we have obtained perchlorates *in ether* in good yield. Cage perchlorates (e.g., **2a,b**), which are more resistant to S<sub>N</sub>2 substitution, can be obtained even *in acetic acid*. However, all the perchlorates studied react rapidly with a variety of nucleophiles (including LiCl) *in acetone* with inversion at carbon.<sup>35</sup>



a, Y = Cl; b, Y = Br; c, Y = OSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-p

We believe that only subsequent S<sub>N</sub>2 reactions have prevented previously obtaining these covalent derivatives, masking the nucleophilicity of the nucleofugal anions. While these products can be preparatively isolated only in those solvents in which S<sub>N</sub>2 processes are suppressed, modern analytical methods will probably permit detection of their transient formation even in more polar media.

Consider now the problem of the nucleophilicity of “nucleofugal” anions. Our data, suggesting an apparent increase of nucleophilicity for ClO<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and similar anions, actually reveal selectivities of salts of nucleofugal anions vs. other nucleophiles. A rough estimation of S<sub>LiClO<sub>4</sub>/AcOH</sub> from preparative experiments gives unbelievable values up to 20! At the same time, there exists a lot of evidence that both AcOH and LiCl are sufficiently nucleophilic to trap carbocationic-like intermediates, e.g., in Ad-E reactions.

To explain the discovered phenomenon, we put forward a hypothesis that *the salts of typical “nucleofugal” anions, being nonnucleophilic in usual S<sub>N</sub>2 reactions, possess pronounced nucleophilic character either toward transient short-lived carbocationic intermediates or in concerted S<sub>N</sub> processes for which transition states closely resemble carbocations.*

Consider some points of this statement. Earlier, we discussed warily our data in terms of “carbocationic-like” intermediates. Indeed, some of the reactions we have considered involve definitely carbocationic intermediates, the appearance of which is manifested in the formation of rearranged structures. On the other hand, some of the reactions, especially those occurring at a primary carbon atom,<sup>37</sup> do not proceed via such an intermediate. They proceed actually via a concerted mechanism through an “open” or “exploded” or “ion-

(36) S. Winstein, L. G. Savedoff, S. G. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, **24** (1960); P. Beronis, U. Isacsson, and A. M. Nilsson, *Acta Chem. Scand.*, **24**, 189 (1970).

(37) d. N. Kevill and H. S. Posselt, *J. Chem. Soc., Perkin Trans.* **2** 909 (1984).

sandwich-like" transition state with substantial positive charge developing on the carbon atom.<sup>6,9</sup>

This assumption means that the apparent nucleophilicity of the "nucleofugal" anions is extremely dependent on carbocationic character of the transition state or on the positive charge on the carbon atom of an intermediate. Such behavior has some analogies. For instance, the relative order of nucleophilicity of  $N_3^-$  vs.  $CN^-$  is dependent on the carbocationic character of the transition state.<sup>9</sup> However, the sensitivity of the "nucleofugal" anions to the development of positive charge on the attacking carbon atom is much more drastically expressed: these anions can play two roles, being either nonnucleophilic species in usual  $S_N2$  reactions or powerful competitive nucleophiles in reactions with pronounced carbocationic character.

Some other factors that undoubtedly are significant are different changes in solvation of "nucleofugal" anions vs. "usual" ones,<sup>18,38,39a</sup> difference in lipophilicities of these anions,<sup>39</sup> and the pronounced proclivity of the "nucleofugal" anions for ion pairing. However, discussion of these points would go beyond experimental evidence now available.

### Concluding Remarks

In conclusion we would like to emphasize two points. First, we have found that a variety of the products are formed by incorporation of "nucleofugal" anions in the final steps of many reactions. It appears that the observed phenomenon represents a significant advance for

synthetic purposes. Furthermore, ramification of this phenomenon has allowed us to design a number of novel reagents<sup>32b</sup> and methods such as  $NO_2^+$ -initiated epoxide ring opening<sup>34</sup> and  $SO_3$ -mediated electrophilic addition of weak electrophiles.<sup>40</sup>

Second, our findings should lead to far more important results. Many modern mechanistic ideas have been extracted from studies of solvolysis reactions. However, an alternative approach to mechanistic problems may be developed; it involves the generation of carbocation-nucleophile ion pairs from separate ions to establish whether or not they give any covalent derivatives.<sup>41</sup>

In establishing that external nucleophiles from an added salt, including *p*-toluenesulfonate and perchlorate ions, can form a covalent product, the corresponding alkyl ester, even in a medium as nucleophilic as acetic acid, we have efficiently demonstrated that carbocationic processes may be accompanied by return from ions to ion pairs of different types and finally to covalent adducts. In turn, this result may require revision or at least modification of mechanistic ideas concerning such phenomena as internal return and the spectral salt effect.

From the foregoing it would appear that exploration of the phenomenon of competitive covalent binding of "nucleofugal" anions complemented with a proper mechanistic understanding will bring a lot of new interesting results.

(40) (a) Addition of weak electrophiles: (1)  $SO_3 + R_2NCl$ , N. S. Zefirov, N. V. Zyk, S. I. Kolbasenko, and A. G. Kutateladze, *Sulfur Lett.*, **2**, 95 (1984); (2)  $SO_3 + RSCl$ , N. S. Zefirov, A. S. Kozmin, V. D. Sorokin, A. V. Schastin, and E. S. Balenkova, *Dokl. Akad. Nauk SSSR*, **276**, 1139 (1984); (3)  $SO_3 + RONO$ , N. S. Zefirov, N. V. Zyk, and A. G. Kutateladze, *Zh. Org. Khim.*, **20**, 5474 (1984). (b)  $Cl_2$  also reacts with  $SO_3$  to give  $ClOSO_2Cl$  and then addition products; N. S. Zefirov, A. S. Kozmin, and V. D. Sorokin, *J. Org. Chem.*, **49**, 4087 (1984).

(41) H. Maskill, J. T. Tompson, and A. A. Wilson, *J. Chem. Soc., Chem. Commun.* 1239 (1981).

(38) D. N. Kevill, *Tetrahedron Lett.*, **24**, 1211 (1983).

(39) (a) R. Alexander, E. C. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, **89**, 3703 (1967). (b) E. V. Dehmlov and S. S. Dehmlov, "Phase Transfer Catalysis", Verlag Chemie, Weinheim/Bergstr., 1980, pp 13-15. (c) D. N. Kevill, M. Banari, and S. W. Anderson, *J. Am. Chem. Soc.*, **106**, 2895 (1984).

# ADDITIONS AND CORRECTIONS

Volume 17, 1984

**Dudley H. Williams:** Structural Studies on Some Antibiotics of the Vancomycin Group, and on the Antibiotic-Receptor Complexes, by  $^1H$  NMR.

Page 364. Reference 26 refers to the X-ray structure of *N*-Ac-L-Ala-L-Ala-L-Ala, and not *N*-Ac-D-Ala-D-Ala. The X-ray structure of the latter compound is published by Benedetti, E.; Di Blasio, B.; Pavone, V.; Pedone, C.; Toniolo, C.; Bonora, G. M. *J. Biol. Chem.* **1981**, *256*, 9229.