describe extensive chemistry based on novel derivatives from hydrogen cyanide chemistry, particularly with DISN as the key intermediate.

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Influence of Remote Functional Groups in the Chemical Ionization Mass Spectra of Long-Chain Compounds

Sir:

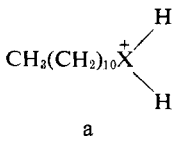
It has been previously demonstrated that the interaction between remote functional groups or atoms in long-chain compounds can lead to major effects in their electron ionization mass spectra.[1] These effects were originally recognized as being due to winding or coiling of the conformationally mobile long chains[2,3] and have more recently been associated with such factors as transition-state ring size,[4] stabilization by charge exchange,[1c] sites of localized activation,[5] and internal solvation by the alkyl chain.[1a,6]

In view of the fundamentally different nature of ions produced by chemical ionization,[7] we have sought to identify the occurrence of remote group participation in the spectra of suitable long-chain models. For these purposes the chemical ionization spectra of monofunctional compounds **1a–c** have been recorded using methane reagent gas, and compared with those of the corresponding bifunctional analogs **2a–c**.[8] Our spectra of **1a** and **1c** are similar to those of 1-decanol and 1-

$CH_3(CH_2)_9XH$ (**1**) $\qquad$ $HX(CH_2)_{10}XH$ (**2**)

a, X = O
b, X = S
c, X = NH

octylamine previously reported.[10] As shown in Table I, the abundances of protonated molecular ions $(M + H)^+$ from the **1** series (ion a) reflect increased stabilization, and therefore less rapid fragmentation, in the order N > S > O, in analogy to the same general order found on electron ionization.[11] The stability of $(M + H)^+$ from **1a** is sufficiently low that no peak is observed,[10] a relatively unusual occurrence for molecules which contain a heteroatom. Earlier studies using the less energetic reagent gas isobutane have shown that the tendency to form $(M + H)^+$ from monofunctional alcohols further decreases with increasing chain length, and no peak is observed with chain lengths greater than C_5.[12]



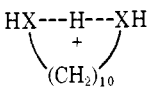
a

Table I. Abundance of $(M + H)^+$ in the Methane Chemical Ionization Mass Spectra of **1** and **2**

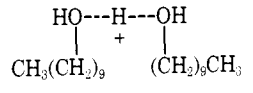
Compound	% rel int	% Σ_{60}[a]
1-Decanol (**1a**)	0.0	0.0
1-Decanethiol (**1b**)	90	23
1-Decylamine (**1c**)	100	73
1,10-Decanediol (**2a**)	59	14
1,10-Decanedithiol (**2b**)	100	51
1,10-Decanediamine (**2c**)	100	88

[a] Excluded from calculation were (i) peaks below *m/e* 60, to avoid contributions from reagent gas, and (ii) peaks representing adduct ions arising from unrelated processes, such as $(M + C_2H_5)^+$.

By contrast, the presence of a second heteroatom at the opposite end of the chain produces marked enhancement of $(M + H)^+$, as indicated by comparisons of **1** *vs.* **2** in Table I. We attribute the increased stabilities of $(M + H)^+$ from the **2** series to proton sharing

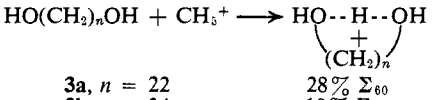


b



c

by the heteroatoms (ion b). The same effect is achieved by operating at high partial pressures of **1a**, which, in parallel to the behavior of CH_3OH,[13] permits formation of clusters of the type $(CH_3(CH_2)_9OH)_nH^+$, where, however, $n = 2$ and 3 but not 1. The stabilized complex shown schematically as c is therefore analogous to ion b, and points to a degree of similarity between ion–molecule reactions and those occurring between the termini of long chains.[14] As the alkyl chain is lengthened (**3a–c**), $(M + H)^+$ still accounts for a significant portion of the total ion current,[15] implying the existence of cyclic ions containing up to 49 members.



3a, $n = 22$ — 28% Σ_{60}
3b, $n = 34$ — 10% Σ_{60}
3c, $n = 46$ — 5.2% Σ_{60}

Hydride abstraction leading to $(M - H)^+$ is significant in the spectra of **1a**,[10] **2a**, and **3**. In **1a**, the α-carbon has been postulated[10] as the point of ab-

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(2) R. Ryhage and E. Stenhagen, *J. Lipid Res.*, **1**, 361 (1960).

(3) J. A. McCloskey and M. J. McClelland, *J. Amer. Chem. Soc.*, **87**, 5090 (1965).

(4) For example, H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 179–180.

(5) For example, S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **88**, 56 (1966); A. Caspar, G. Teller, and R. E. Wolff, *Org. Mass Spectrom.*, **3**, 1351 (1970).

(6) P. Bommer and K. Biemann, *Annu. Rev. Phys. Chem.*, **16**, 481 (1965).

(7) F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

(8) Determined on a CEC 21-110B instrument, modified as previously described:[9] P_{CH_4}, 0.4 Torr; ion source temperatures, 120–150°; accelerating voltage, 8 kV; repeller field, 0–30 V/cm.

(9) I. Dzidic, D. M. Desiderio, M. S. Wilson, P. F. Crain, and J. A. McCloskey, *Anal. Chem.*, in press.

(10) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **88**, 2621 (1966).

(11) K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, N. Y., 1962, p 87.

(12) F. H. Field, *J. Amer. Chem. Soc.*, **92**, 2672 (1970).

(13) M. S. B. Munson, *ibid.*, **87**, 5313 (1965).

(14) This similarity was first pointed out to us in the case of electron ionization spectra of α,ω-bis(trimethylsilyl) ethers, by Dr. F. H. Field (personal communication, Jan 1970).

(15) Compounds **3a**, **3b**, and **3c** were introduced by direct probe, at ion source temperatures of 180, 220, and 250°, respectively.

straction, leading to the well-stabilized ion d, based on

$$CH_3(CH_2)_8\overset{+}{C}H{=}\overset{+}{O}H$$
d, $(M - H)^+$

two factors: (1) strong attraction of the attacking reagent ions to the site of the polar group due to dipole interactions, (2) the absence of $(M - H)^+$ in the spectra of tertiary alcohols which bear no α-hydrogens.[1,2] To test this hypothesis we examined the chemical ionization spectra of **1a**-*1,1-d*$_2$ and **2a**-*1,1,10,10-d*$_4$, and found that only 10 (**1a**) and 3% (**2a**) of the hydrogen lost originates from the α positions (neglecting isotope effects). The values expected from statistically random abstraction are 9.5 and 4%, respectively. Although these results seem to oppose the concept of localized attack at the site of the polar group, a reasonable explanation may lie in the proposal, convincingly developed by Meyerson,[1a] that the functional group is internally solvated by the polymethylene chain, and hence is surrounded by a number of other eligible alkyl hydrogens at the time of attack by the reagent ion. In addition, the ratio of abundances $(M - H)^+/(M + H)^+$ on a % Σ_{60} basis increases with chain length (**2a**, 0.16; **3a**, 0.81; **3b**, 1.7; **3c**, 2.2), which also reflects decreased influence of the polar hydroxyl group in favor of the alkyl chain.

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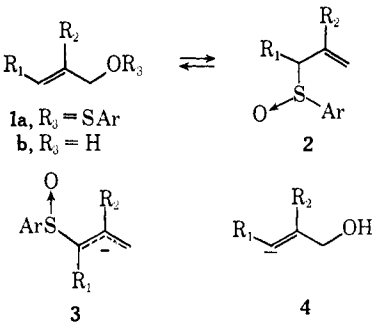
Reversible 1,3 Transposition of Sulfoxide and Alcohol Functions. Potential Synthetic Utility

Sir:

Synthetic operations which serve to "reverse" the normal reactivity of a functionalized carbon moiety have received scant attention.[1] However, as has been pointed out, this class of transformations holds forth great promise as a general manipulative operation which may create added flexibility in synthesis.[2] Herein we wish to illustrate the synthetic utility and scope of the *completely reversible* 1,3 transposition of sulfoxide and alcohol functions, the overall transformation being represented by eq 1. A representative demonstration of the flexibility that such a functional group interconversion creates is illustrated by the synthetic equivalence of the sulfoxide-stabilized anion **3** and the hypothetical vinyl anion **4**.[3]

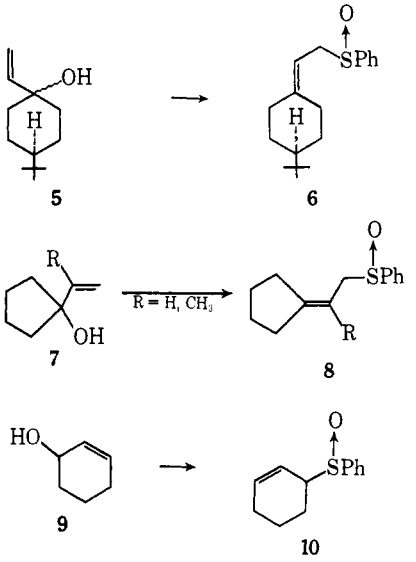
Recently, Mislow and coworkers have demonstrated that simple allylic alcohols such as **1b** (R_1, R_2 = H; R_1 = CH_3; R_2 = H), on conversion to the corresponding lithium alkoxides followed by treatment with aryl-



(1)

sulfenyl chlorides, may be smoothly transformed *via* the sulfenate esters **1a** into the rearranged allylic sulfoxides **2**,[4,5] this isomerization being a typical example of the generalized class of [2,3]-sigmatropic rearrangements.[6] As part of our general plan to utilize this rearrangement in synthesis we have demonstrated, indeed, that this reaction appears to be general and proceeds in excellent yields for the structurally diverse alcohols shown below (Scheme I). In the cases illustrated, the conversion of alcohol into rearranged sulfoxide may be executed in isolated yields in excess of 80% using conditions similar to those reported.[7]

Scheme I



The reverse transformation, *i.e.*, that of sulfoxide **2** into rearranged allylic alcohol **1b**, is highly desirable if the former function is to be employed as a temporary activating group in synthesis. We have shown that this transfer of functionality may be readily accomplished by simply heating the allylic sulfoxide in the presence of a suitable thiophile.[8] The allylic sulfenate esters (*e.g.*, **1a**), although usually present in low equilibrium concentration with the isomeric sulfoxides,[4,5] may be efficiently trapped by thiophenoxide to afford the rearranged allylic alcohols in good yields. Although the interception of an allylic sulfenate ester generated as a result of a [2,3]-sigmatropic process has

(1) D. Seebach, *Synthesis*, 17 (1969); E. J. Corey, B. W. Erickson, and R. Noyori, *J. Amer. Chem. Soc.*, **93**, 1724 (1971).
(2) E. J. Corey, *Pure Appl. Chem.*, **14**, 19 (1967).
(3) This equivalence is only possible if **3** reacts at the α rather than the γ position relative to the sulfoxide function.
(4) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4869 (1968), and references cited therein.
(5) R. Tang and K. Mislow, *ibid.*, **92**, 2100 (1970).
(6) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.*, 538 (1968).
(7) As a minor modification we use THF as a solvent and add the sulfenyl chloride to the alkoxide at −50°.
(8) A. J. Parker and N. Kharasch, *Chem. Rev.*, **59**, 583 (1959).