A Novel McLafferty Rearrangement of Alkyl Sulfinyl Amines

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The problem of geometrical isomerism associated with N-substituted sulfinyl amines has received little attention except that we predicted that *N*-methylsulfinyl amine is more stable trans than cis by 13 kcal/mol.[1] We now report the mass spectral data, which give evidence for the validity of this prediction.

Recently, the mass spectra of several aryl sulfinyl amines showed significant migration of the aryl group from nitrogen to oxygen.[2] We do not find this rearrangement in the spectra of alkyl sulfinyl amines.

The mass spectra of di-*tert*-butylsulfur diimide and di-*n*-butylsulfur diimide reveal a double McLafferty rearrangement giving an ion at *m/e* 62 ($HN^+{=}S{=}NH$),[3] but *N*-alkyl sulfinyl amines do not fragment to give an ion at *m/e* 63 ($HOS^+{\equiv}N$). This latter result suggests that the alkyl group is trans to oxygen in the sulfinyl amines. A general scheme for the fragmentation pattern of sulfinyl amines is presented in Scheme I. The molecular ions are in low abundance compared to the aryl derivatives.

N-1-Butylsulfinylamine radical cation ($R^I = R^{II} = R^{III} = R^{IV} = R^V = H$; $R^{VI} = CH_3$) suffers the loss of propene to form the ion *m/e* 77 (pathway f) while the *N*-2-butylsulfinylamine cation ($R^I = CH_3$; $R^{II} = R^{III} = R^{IV} = R^V = R^{VI} = H$) loses ethylene to form the ion *m/e* 91. Fragmentation of the cation of *N*-3-methyl-1-butylsulfinylamine ($R^V = R^{VI} = CH_3$; $R^I = R^{II} = R^{III} = R^{IV} = H$) gives an ion *m/e* 77 and the cation of *N*-2-pentylsulfinylamine ($R^I = R^{VI} = CH_3$; $R^{II} = R^{III} = R^{IV} = R^V = H$) fragments to an ion at *m/e* 91.

These ions arise *via* a McLafferty rearrangement in which hydrogen is abstracted from the γ-carbon atom by sulfur as shown in Scheme I by step f. However, when the α-carbon atom is highly substituted, then simple cleavage of the α,β carbon–carbon bond is more prominent than the McLafferty rearrangement just mentioned. This cleavage (pathway a) is exemplified by *N*-1,1-dimethyl-1-propylsulfinylamine ($R^I = R^{II} = CH_3$; $R^{III} = R^{IV} = R^V = R^{VI} = H$), which loses an ethyl group to form an ion at *m/e* 104, the most abundant ion in the spectrum. The same ion is the result of the most important fragmentation of *N*-2-methyl-2-propylsulfinylamine.

However, when the β carbon is highly substituted, then the positive charge becomes associated with the alkyl fragment (pathway b), a pattern which is shown by *N*-2,2-dimethyl-1-propylsulfinylamine ($R^I = R^{II} = R^V = R^{VI} = H$; $R^{III} = R^{IV} = CH_3$) giving the *tert*-butyl cation as the base peak. Pathway c is only important for *N*-3-methyl-1-butylsulfinylamine.

(1) J. R. Grunwell and W. C. Danison, *Tetrahedron*, **27**, 5315 (1971).
(2) J. H. Bowie, F. C. V. Larsson, G. Schroll, S.-O. Lawesson, and R. G. Cooks, *Tetrahedron*, **23**, 3743 (1967).
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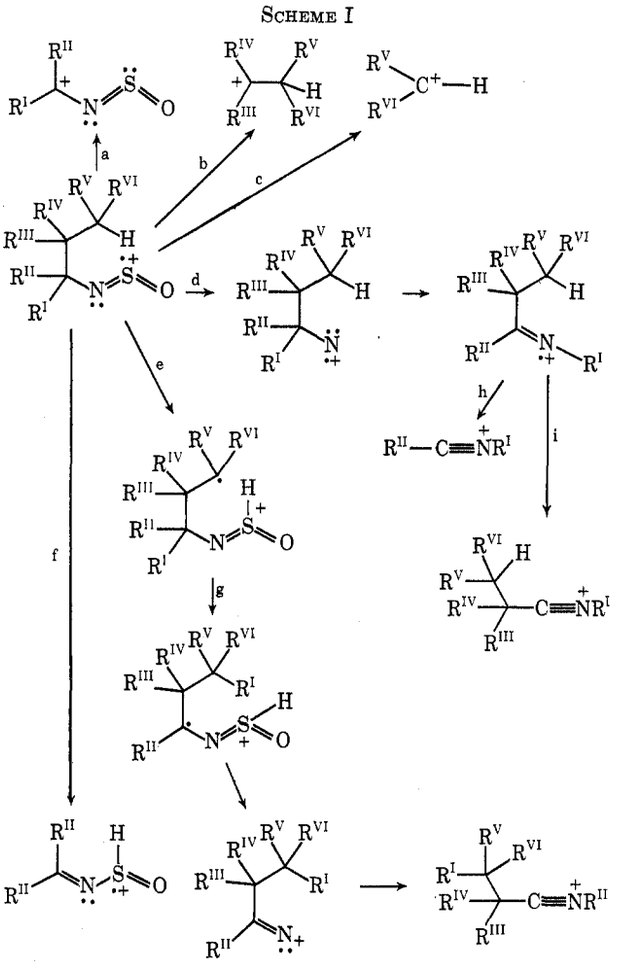
SCHEME I



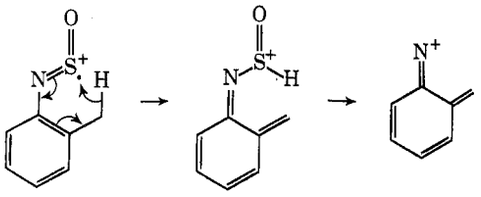
Another important fragmentation pathway involves the initial loss of sulfur monoxide. For example, *N*-2-butylsulfinylamine forms an ion at *m/e* 71 which subsequently fragments to ions at *m/e* 56 and 42 by cleavage of methyl and ethyl radicals, respectively. This pathway is represented by steps d to i and h. The same process occurs in *N*-2-pentylsulfinylamine, except that the ion at *m/e* 85 fragments to *m/e* 70 and 42 by loss of methyl and propyl radicals.

Some of the sulfinylamines, particularly those which undergo an efficient McLafferty rearrangement, suffer loss of the elements of HS=O as represented by step g following e. *N*-1-Butylsulfinylamine shows a prominent peak at *m/e* 70, while *N*-3-methyl-1-butylsulfinylamine gives an ion at *m/e* 84.

When the alkyl group of a sulfinyl amine is trans to the oxygen atom, then the rearrangement shown in step f of Scheme I may occur. In analogy with the mass spectrum of bis-*tert*-butylsulfur diimide (**1**) (the nmr spectrum[4] of **1** at $-40°$ is two peaks of equal intensity showing that one *tert*-butyl group is cis), an ion at *m/e* 63 ($HOSN^+$) may be expected if the alkyl group is cis to the oxygen of a sulfinyl amine. None of the sulfinyl amines exhibit a peak at *m/e* 63, while several of them fragment according to mechanism f. These observations suggest that the alkyl group of sulfinyl amines is trans. Further, *N*-1-butylsulfinylamine does not pyrolyze to 1-butene, which is the product of the pyrolysis of the corresponding sulfur diimide.[4]

(4) J. R. Grunwell, J. A. Rieck, and C. Hoyng, unpublished results.

In view of the observed McLafferty rearrangement, the loss of the elements HS=O from 2-methylsulfinylaniline may be reinterpreted in terms of trans isomer (eq 1).



(1)

Although the molecular ions were in extremely small abundance, the nmr spectra and elemental analyses provide convincing evidence that the sulfinylamines are pure. The nmr spectrum of *N*-2,2-dimethyl-1-propylsulfinylamine showed a singlet resonance at δ 3.8 ppm for the methylene protons on carbon adjacent to nitrogen. This signal did not split or broaden at $-100°$, so that if rapid interconversion between trans and cis isomers is occurring at room temperature it should be slowed sufficiently at $-100°$ to observe two signals unless the cis isomer is a maximum on the rotational potential surface or is much less stable than the trans isomer. Also, *N*-2-methyl-2-propylsulfinylamine has a singlet proton resonance at δ 1.50 ppm which does not change at $-100°$.

Experimental Section

All mass spectra were measured with a Hitachi Perkin-Elmer RMU-6 mass spectrometer operating at 70 eV and with the inlet system at 200°. All nmr spectra were measured with a Jeolco C-60H spectrometer with TMS as the internal reference (δ = 0.00 ppm). Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

General Procedure. Synthesis of Sulfinyl Amines.— Sulfinyl amines were prepared by the method described by Michaelis and Stornbeck[5] by adding thionyl chloride (0.095 mol in 75 ml of ether) to the appropriate alkyl amine (0.29 mol in 100 ml of ether) maintained at 0° for 1 hr. The ether was filtered and then removed by distillation at atmospheric pressure. The remaining residue is placed on a high vacuum line (10^{-5} mm) and fractionated through three traps maintained at $-45°$ (chlorobenzene slush), $-77°$ (Dry Ice–acetone), and $-196°$ (liquid N_2). Pure sulfinyl amine was obtained from the $-45°$ trap by distilling into bulbs fitted with a stopcock for all mass spectral samples, into nmr tubes which were sealed off under vacuum, and into 3-mm tubing sealed under vacuum for all analytically pure samples. A satisfactory analysis could not be obtained for *N*-3-methyl-1-butylsulfinylamine because this compound suffers a mysterious decomposition at room temperature within 0.5 hr, turning yellow and finally solid after a couple of days.

N-1-**Butylsulfinylamine**[6] had mass spectrum (70 eV) *m/e* (rel intensity) 77 (89), 76 (14), 75 (11), 71 (14), 70 (54), 55 (11), 50 (13), 43 (100), 42 (16), 41 (86), 39 (23), 30 (13), 29 (35), 27 (65).

N-2-**Butylsulfinylamine** had mass spectrum (70 eV) *m/e* (rel intensity) 104 (5), 91 (58), 90 (100), 89 (17), 71 (28), 70 (11), 63 (14), 60 (20), 57 (15), 56 (35), 55 (11), 44 (53), 43 (49), 42 (71), 41 (44), 39 (17), 29 (61), 27 (54); nmr δ (multiplicity) 0.90 (3 H, t, J = 7.0 Hz), 1.33 (3 H, d, J = 7.0 Hz), 1.50 (2 H, q, J = 7.0 Hz), and 4.73 (1 H, sextet, J = 7.0 Hz).

Anal. Calcd for C_4H_9NSO: C, 40.31; H, 7.61; N, 11.76; S, 26.90. Found: C, 40.43; H, 7.68; N, 11.47; S, 26.77.

N-2-**Methyl-2-propylsulfinylamine**[7] had mass spectrum (70 eV) *m/e* (rel intensity) 104 (100), 74 (12), 57 (49), 56 (19), 42 (17), 41 (60), 39 (15), 29 (22), 27 (13); nmr δ (multiplicity) 1.50 (9 H, s).

N-2-**Pentylsulfinylamine** had mass spectrum (70 eV) *m/e* (rel intensity) 91 (78), 90 (34), 89 (14), 70 (34), 56 (11), 55 (19), 43 (100), 42 (53), 41 (55), 39 (24), 29 (20), 27 (47); nmr δ (multiplicity) 0.90 (3 H, t, J = 7.0 Hz), 1.00 (2 H, q, J = 7.0 Hz), 1.22 (3 H, d, J = 7.0 Hz), 1.47 (2 H, q, J = 7.0 Hz), 4.83 (1 H, sextet, J = 7.0 Hz).

Anal. Calcd for $C_5H_{11}NSO$: C, 45.08; H, 8.33; N, 10.51; S, 24.07. Found: C, 45.30; H, 8.43; N, 10.33; S, 23.90.

N-3-**Methyl-1-butylsulfinylamine** had mass spectrum (70 eV) *m/e* (rel intensity) 85 (17), 84 (24), 77 (74), 76 (19), 69 (16), 57 (63), 55 (36), 43 (80), 42 (26), 41 (100), 39 (33), 30 (16), 39 (70), 27 (40); nmr δ (multiplicity) 0.93 (6 H, d, J = 6.0 Hz), 1.57 (3 H, m), and 3.97 (2 H, t, J = 7.0 Hz). A satisfactory analysis was not obtained.

N-1,1-**Dimethyl-1-propylsulfinylamine** had mass spectrum (70 eV) *m/e* (rel intensity) 104 (100), 74 (17), 71 (13), 56 (12), 55 (20), 43 (29), 42 (34), 41 (34), 40 (17), 39 (15), 31 (10), 29 (14), 27 (46); nmr δ (multiplicity) 0.93 (3 H, t, J = 7.0 Hz), 1.47 (3 H, s), and 1.73 (2 H, q, J = 7.0 Hz).

Anal. Calcd for $C_5H_{11}NSO$: C, 45.08; H, 8.33; N, 10.15; S, 24.07. Found: C, 44.95; H, 8.40; N, 10.37; S, 23.85.

N-2,2-**Dimethyl-1-propylsulfinylamine** had mass spectrum (70 eV) *m/e* (rel intensity) 118 (3), 77 (4), 76 (3), 57 (100), 55 (13), 41 (47), 39 (14), 29 (35), 27 (12); nmr δ (multiplicity) 1.00 (9 H, s), 3,80 (2 H, s).

Anal. Calcd for $C_5H_{11}NSO$: C, 45.08; H, 8.33; N, 10.51; S, 24.07. Found: C, 45.25; H, 8.42; N, 10.39; S, 24.01.

Registry No.—*N*-1-Butylsulfinylamine, 13165-70-3; *N*-2-butylsulfinylamine, 13165-71-4; *N*-2-methyl-2-propylsulfinylamine, 38662-39-4; *N*-2-pentylsulfinylamine, 38662-35-0; *N*-3-methyl-1-butylsulfinylamine, 38662-36-1; *N*-1,1-dimethyl-1-propylsulfinylamine, 38662-37-2; *N*-2,2-dimethyl-1-propylsulfinylamine, 38662-38-3.

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Studies in the 1,4-Diphosphoniacyclohexadiene System. New Organophosphorus Heterocycles[1]

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Some years ago it was found that alkynyl-1-phosphines **1** and **2** on treatment with HBr (or HCl) in glacial acetic acid produce the endocyclic dienes **3** and **4**, respectively (eq 1 and 2).[2-4] The endocyclic dienes **3** (R = primary or secondary alkyl) were found to readily isomerize on heating to the exocyclic dienes **5**;[3] however, unlike the P-phenylated dienes **3**, the P-alkylated dienes **4** failed to thermally isomerize to the corresponding P-alkylated exocyclic dienes **6** (eq 1 and 2).[4]

(1) Abstracted in part from the Ph.D. Dissertation of M. S. Chattha, Tulane University, New Orleans, La., 1971.

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