Table III

R	CF_3•	CF_3CH_2•	CH_3•	FCH_2•	HCF_2•	$ClCH_2$•	$HCCl_2$•	CCl_3•
k_{rel} (1, 160 °C)	0.09	0.52	1.0	8.6	9.5	–	59	62
k_{rel} (2, 140 °C)	0.08	–	1.0	9.0	10.2	22	–	–

Recently, there have been quite a number of examples which show that two substituents directly bonded to the radical center usually do not lead to an additive effect on the stability of the radical. Some authors have suggested that it can be either synergistic or antagonistic, depending on whether the two substituents are of opposite or similar polarity.[10] To our knowledge, however, there is no previous report which demonstrates that the nature of the substituent effect can be completely reversed by increasing the number of the same substituent.

Although many reports imply that monochlorine substitution stabilizes a radical,[8] there appears to be no direct experimental data on di- and trichloromethyl radicals. Our results show that the stabilizing effect of α-chlorine substitution progressively increases with the number of the chlorine substituent. However, it is noteworthy that the second chlorine makes its presence strongly felt, but the effect of the third chlorine is rather small.

The α-CF_3 substituent appears to exert a slightly destabilizing effect on the methyl radical. The small difference of k_{rel} values between CF_3CH_2• and CH_3• could also be a reflection of a very week ground-state polar effect on the strengths of the R–CMe_2O• bonds.[11] The σ• values and other data suggest that the effect of the α-CF_3 group is either negligible or slightly destabilizing.[8,9]

It is interesting to note that Pasto's most recent theoretical calculations[12] predict the following order of relative stabilities:

$$CF_3^\bullet < CF_3CH_2^\bullet < CH_3^\bullet < HCF_2^\bullet < FCH_2^\bullet < ClCH_2^\bullet < HCCl_2^\bullet < CCl_3^\bullet$$

It is qualitatively in good agreement with our experimental results.

Registry No. **1a**, 123359-21-7; **1b**, 123359-22-8; **1e**, 123359-23-9; **1g**, 123359-24-0; **2a**, 123359-25-1; **2b**, 123359-26-2; **2d**, 123359-27-3; **3a**, 123359-28-4; **3b**, 123359-29-5; **3d**, 42334-92-9; **3e**, 123359-30-8; **3g**, 123359-31-9.

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A Reliable Method for Fast Atom Bombardment Mass Spectrometric Analysis of α-Aryl 1,2-Diols. Formation of Lithium–Diol Adducts

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Summary: An operationally simple and reliable method for obtaining molecular ion information on α-aryl 1,2-diols using fast atom bombardment mass spectrometry is described. Analysis entails formation of lithium–diol adducts using a solution of LiCl and matrix solvent and then bombarding the sample with either xenon atoms or cesium ions to afford $[MLi]^+$ ions.

Sir: The analysis of 1,2-diols by electron impact mass spectrometry (EIMS) has always been troublesome.[1] In general, these compounds give rise to little or no molecular ion using this technique. A general remedy for this problem has been chemical derivatization of the bifunctional group. However, this necessitates an additional synthetic step as well as ensuring that nothing happens to the product upon derivatization (e.g. decomposition, rearrangement, etc.). Many elegant studies concerning stereochemical effects in the chemical ionization mass spectra (CIMS) of diols have been reported.[2] One drawback of this technique is that like EIMS, the compounds being analyzed must be sufficiently volatile to allow for vaporization in vacuo. Fast atom bombardment mass spectrometry (FABMS) is commonly used to obtain molecular ion and structural information on polar molecules and therefore seemed perfectly suited for the analysis of a range of vicinal diols. However, during the course of a project involving the development of an efficient method for coupling two different carbonyls (pinacol cross coupling)[3] we found that FABMS analysis of α-aryl 1,2-diols does not always provide molecular ion information. Herein we present a practical method for the analysis of such diols via FABMS which involves formation of a lithium–diol complex.

The detection of protonated molecular ions ($[MH]^+$) in the FABMS of 1,2-diaryl-1,2-ethanediols (**1**), 1-aryl-2-alkyl-1,2-ethanediols (**2**), and 1-aryl-1,2-dialkyl-1,2-ethanediols (**3**) was only moderately succesful employing a range of matrices. In general, compounds **1** and **3** gave no molecular ion information whereas compounds **2** produced variable results. The major difficulty in the analysis of compounds **1**, **2**, and **3** is the instability of the protonated molecular ion with respect to loss of water (i.e. $[MH - H_2O]^+$ is always observed).[4] We felt that replacing the

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[2] Mandelbaum, A. *Mass Spectrom. Rev.* **1983**, *2*, 223.

[3] (a) Freudenberger, J. H.; Konradi, A. W.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 8014. (b) Freudenberger, J. H.; Konradi, A. W.; Takahara, T.; Pedersen, S. F. *Tetrahedron Lett.* Submitted.

[4] Similar results are observed in the CIMS of 1,2-diols.

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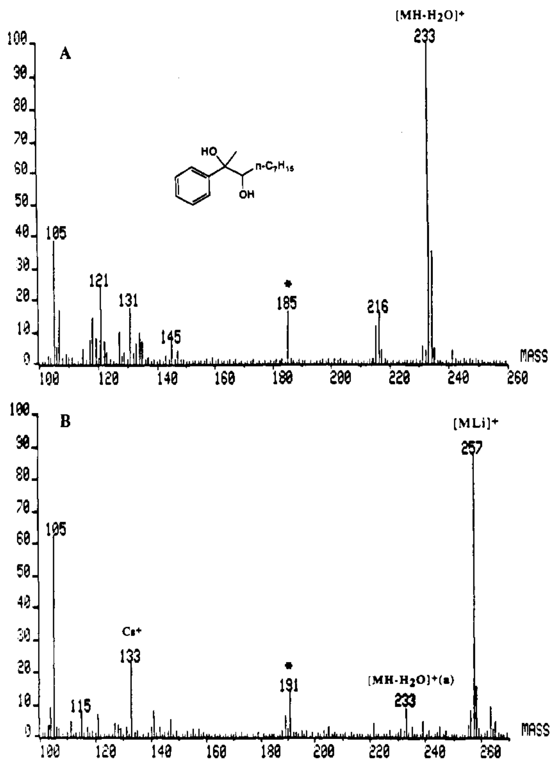

Figure 1. (A) Low-resolution FABMS of a 1:1 (threo:erythro) mixture of 2-phenyl-2,3-decanediol in a thioglycerol/glycerol matrix. (B) Low-resolution FABMS of 2-phenyl-2,3-decanediol in a thioglycerol/glycerol matrix after treatment with LiCl. The ion at m/z 133 comes from the cesium ion gun. (a) See reference 14 for an explanation of this ion. *Matrix and lithium-matrix ion in A and B, respectively.

additional proton with an alkali metal ion would result in the formation of a chelated complex[5,6] that should be more stable than an $[MH]^+$ ion.[7] Alkali metal impurities are often detected in the FABMS of polar molecules and show $[M + metal]^+$ ions.[8] More recently such metals have been purposely used in the detailed analysis of peptides.[9]

We chose to begin these studies with the lithium ion due to some previous work carried out by one of us.[10] A typical procedure involves dissolving or suspending either **1**, **2**, or **3** (less than 10 μg) in aqueous LiCl (0.07 M; 5 μL) and diluting with an equal volume of either 3-nitrobenzyl alcohol or a mixture of thioglycerol/glycerol (1:1) (5 μL).[11] The solution was agitated on a vortex mixer for several seconds, and then a portion (ca. 1 μL) was applied to a stainless steel probe tip. Analysis was carried out by bombarding the matrix mixture with either xenon atoms or cesium ions,[12] which led to the formation of abundant $[MLi]^+$ ions (Figure 1).[13] We have also used this procedure to analyze non-α-aryl 1,2-diols in cases where normal FABMS conditions gave little or no molecular ion information. Over 30 acyclic vicinal diols have been analyzed using this procedure. Stereochemical effects in the FABMS of metal-diol adducts as well as the use of metal ions in the mass spectrometric analysis of carbohydrates and related materials are in progress.

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(5) For examples of alkali metal-diol complexes, see: (a) Kniep, R.; Welzel, W.; Weppner, W.; Rabenau, A. *Solid State Ionics*, **1988**, *28-30*, 1271. (b) Ballard, R. E.; Haines, A. H.; Norris, E. K.; Wells, A. G. *Angew. Chem.* **1974**, *86*, 555.

(6) Conformational properties will play an obvious role in the formation of such chelate structures.

(7) Loss of metal hydroxide seems unfavorable.

(8) Martin, S. A.; Costello, C. E.; Biemann, K. *Anal. Chem.* **1982**, *54*, 2362.

(9) Leary, J. A.; Williams, T. D.; Bott, G. *Rap. Commun. Mass Spec.* **1989**, *3*, 192 and references therein.

(10) Leary, J. A.; Tolun, E. *Proceed. 36th Annual Conf. on Mass Spectrom. Allied Topics* **1988**, 779.

(11) Both matrices worked equally well in assisting production of the $[MLi]^+$ ions; the only difference being the background matrix ions observed at different masses.

(12) The experiments were performed using either a xenon atom gun (7 kV with 1.0 μA emission current) or a cesium ion gun (20 kV with 1.5 μA emission current).

(13) All FABMS data were obtained using either a Kratos MS-50 (Kratos, Greater Manchester, U.K.) or a VG ZAB2-EQ mass spectrometer (VG Analytical Ltd, Greater Manchester, U.K.). Single-scan data were collected and processed on either a DS-55 (Kratos) or an 11-250J (VG) data system. Resolution was measured at 1:1000 with 8 kV accelerating voltage.

(14) Tandem mass spectrometry (MS/MS) experiments on $[MLi]^+$ have demonstrated that this ion is not arising from loss of LiOH from $[MLi]^+$. Therefore, it must be derived from unlithiated diol as in Figure 1A. Incomplete adduct formation may be due to insufficient solubility of the diol and/or conformational differences associated with the two possible diastereomeric lithium-diol adducts (we began with a 1:1 mixture of diastereomeric diols).

Generation of Synthetic Equivalents of $RCH(Li)NH_2$ for the Synthesis of Primary Amines. Tin-Lithium Exchange on Carbamate-Protected (α-Aminoalkyl)stannanes

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Summary: N-Alkylation of *N*-benzylcarbamates with (α-iodoalkyl)stannanes provided carbamate-protected (α-aminoalkyl)stannanes **1** and **11**. Tin-lithium exchange with an alkyllithium reagent produced nitrogen-substituted carbanions **7**, which reacted with electrophiles to provide adducts **8** and **12**. Deprotection by transfer hydrogenolysis then produced primary amines **9**.

Sir: The generation and utilization of nitrogen-substituted carbanions continues to be an active area of research and has had a major impact on the synthesis of amines by carbon-carbon bond-forming reactions at nitrogen-bearing carbon. Synthetic equivalents of α-metalated primary, secondary, and tertiary amines have been reported, and are covered in excellent reviews by Beak.[1] We report that

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