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The β-Nitroxyalkyl and β-Sulfonatoxyalkyl Radical Rearrangements

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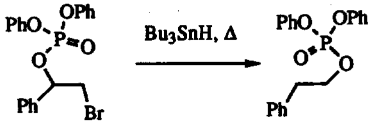
Abstract: The first examples of the migration of nitrate and sulfonate esters in β-nitroxyalkyl and β-sulfonatoalkyl radicals are presented: crossover and labelling experiments are used to determine the migrating group and the intramolecular nature of the rearrangement.

Recently, we described[1] the first examples of the β-phosphatooxyalkyl radical rearrangement (Scheme 1). The close analogy of this reaction with the well known β-acyloxyalkyl radical migration[2,3] and the allylhydroperoxy radical migration[4,5] as well as with the relatively unfamiliar acyloxyalkylsilyl[6] and allylnitroxyl migrations[7] prompted us to search for other examples of what we consider to be a general class of radical rearrangements described by the formalism of Scheme 2.

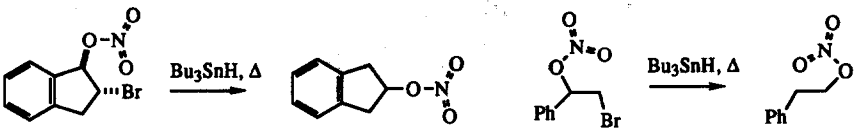


Scheme 1

Scheme 2

Likely candidates for further examples appeared to be β-nitroxy- and β-sulfonatoxyalkyl radicals. We report here that these two classes of radical do indeed undergo the predicted rearrangement.

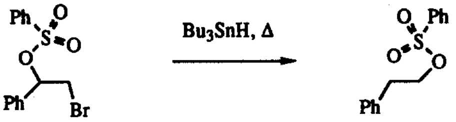
Reaction of indene and styrene bromohydrins with fuming nitric acid/acetic anhydride according to the general procedure described by Honeyman and Morgan[8] gave the β-bromonitrate esters **1** and **2** respectively. Dropwise addition of tributyltin hydride (TBTH) over approx 8 h[9] to refluxing solutions of **1** and **2** in benzene under nitrogen gave the anticipated rearrangement products **3** and **4**, essentially quantitatively, as determined by ^{1}H-NMR analysis of the crude reaction mixtures (Scheme 3). The identity of **3** and **4** was confirmed by comparison with the spectra of authentic samples. A crossover experiment in which **1** was treated with TBTH in the presence of styrene did not lead to the formation of **4** and so indicated an intramolecular rearrangement. Both compounds **1** and **2** were stable to prolonged reflux in benzene in the absence of TBTH so confirming that the rearrangement does not occur by thermal isomerization to the regioisomer followed by simple TBTH reduction. A labelling experiment, in which α-deuterio-**2** was allowed to react with TBTH, eliminated the possibility that **4** was formed by a neophyll rather than nitroxy migration.



1 **3** **2** **4**

Scheme 3

Reaction of styrene bromohydrin with benzenesulfonyl chloride gave the β-bromosulfonate **5**. This compound was unstable to reflux in benzene decomposing to a complex mixture although significantly not to its regioisomer 2-benzenesulfonyloxy-1-bromo-1-phenylethane. In view of this instability the radical reaction was conducted with photochemical initiation in a circulating cold water bath (8 °C). The migration product **6** was formed again essentially quantitatively (Scheme 4). A labelling experiment was again used to prove that the product did not arise from a neophyll rearrangement.[10]



5 **6**

Scheme 4

It is clear from the above experiments that two further cases of the general rearrangement type decribed in Scheme 2 have been identitfed. The two new classes of examples serve to encourage us in our belief that this type of rearrangement is more general than was perhaps previously recognized. We are currently searching for other, and more preparatively useful, instances of this class of rearrangement upon which we will report in due course.

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10. Unfortunately the benzenesulfonate derived from indene bromohydrin has proven too unstable for us to conduct meaningful experiments.

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