TETRAHEDRON REPORT NUMBER 33

RECENT DEVELOPMENTS IN SULFONE CHEMISTRY

PHILIP D. MAGNUS

Evans Laboratory, Department of Chemistry, The Ohio State University, Columbus, OH 43210, U.S.A.

(Received in UK for publication 16 March 1977)

I. INTRODUCTION

The decade from 1966 to 1976 has witnessed an impressive number of original publications devoted to the understanding and applications of organosulfur chemistry. Many highly imaginative syntheses have frequently made use of the unusual and diverse properties of sulfur. Only recently have theoretical organic chemists applied their methods to a more detailed and quantitative understanding of the bonding involvement of sulfur in its various oxidation states. It would be no exaggeration to say that even despite the vast and constantly expanding numbers of publications dealing with sulfides, sulfoxides, sulfones, and various derivatives, much of the chemistry in this area remains unpredictable compared with that of first row analogs. Correspondingly the chemistry of organoselenium and organotellurium compounds is even less predictable.

Turning to the current state of understanding of sulfone chemistry, it is instructive to recall that although the sulfone functional group has been a standard part of organic chemistry for more than a century, it is only within the last few decades that a more diverse range of chemistry has been discovered. It is the intention of this article to describe some of the more important reactions that involve or owe their origin to the sulfone functional group. The sulfone group, in this review is defined as 1; the adjacent carbon atoms may be attached to any functional groups. The emphasis will be to accentuate the synthetic uses of the sulfone group rather than its physical organic chemistry, although germane to this selection will be a brief outline of the more theoretical aspects, which are of course fundamental to any proper appreciation of sulfone chemistry. Finally, it is hoped that whilst the sulfone functional group is associated with a high degree of thermodynamic stability, thus suggesting a lack of ready manipulation, this review will encourage synthetic organic chemists to include sulfone chemistry in their repetoir of synthetic ideas.



II. THEORETICAL ASPECTS OF THE SULPONYL GROUP AND THE & SULFONYL CARBANION

A problem that has caused much discussion amongst both theoretical and synthetic organic chemists is the degree of d₂-p₂ overlap that can occur, and consequently stabilize, ylides of the general type 2; where Z is usually a second row element (S, P, etc.) in various states of oxidation. In particular for our purposes the question is addressed to the α -sulfonylcarbanion 2, Z = SO₂R, which can formally be considered as an ylide, but whose chemistry more typically resembles that of an anion.¹ An intriguing and unexpected property of the α -sulfonyl carbanion 2 $Z = SO_2R$, is that it can be generated in an asymmetric form and retain its asymmetry under a variety of conditions.² Two explanations have been suggested to rationalize this behavior. The α -sulfonylcarbanion may be pyramidal with a high barrier to inversion, or it may be planar with a high barrier to rotation. Elegant experimental evidence has shown that proton transfer to the α -sulfonylcarbanion takes place specifically syn- to the two oxygen atoms.³ More recently MO calculations on the somewhat simplified system -CH₂SO₂H have provided an energy surface as a function of θ and ϕ 3. Of the various possibilities 4a-e it was found that the pyramidal carbanion with the lonepair bisecting the O-S-O angle, 4a, has the lowest energy. Furthermore the d-orbitals do not contribute to the stabilization of the carbanion, and only inductive effects need be engendered.4 The latter conclusion was also reached for calculations concerning the electron deficiency of α . β -unsaturated sulfones.' The planar carbanion 4d was calculated to be some 2.5 kcal mole.¹ less stable than 4a, which in turn is some 4.1 kcal mole⁻¹ more stable than 4b. Experimentally it may be that the energy differences between 4a-c are less than calculated; a value of 1.1 kcal mole 1 was arrived at by considering the rate of exchange of diastereotopic protons α - to a sulfonyl group.⁶ The α -sulfonyl carbanion can in constrained situations, such as thietan derivatives, be forced to take on a planar conformation.

In conclusion it appears that at the present state of theory one need not evoke the 3d-orbitals to explain the asymmetry and stability of the α -sulfonylcarbanion. The asymmetric structure appears to be a consequence of the stereochemical requirements of the two adjacent electron pairs, or an electron pair and adjacent dipole. This is not the end of the story since 3 represents the simplest model of the α -sulfonylcarbanion and the conclusions can only be extended to other systems with extreme caution. Consequently whilst progress has been made in defining the structure of the asymmetric α -sulfonylcarbanion it would be rash to say the problem is now solved.



III. THE RAMBERG-BACKLUND REACTION

Perhaps the most well known and extensively studied reaction involving the sulfone functional group is the Ramberg-Bäcklund reaction. First discovered in 1940⁸ it has been intensively researched by a number of workers.^{9,10} A monograph on the Ramberg-Bäcklund reaction and all its ramifications is soon to be available,¹¹ and as a consequence this section will only discuss those aspects that convey its general synthetic utility. A brief outline of the current status of the mechanism is included.

The most useful feature of the Ramberg-Bäcklund reaction is its intrinsic mechanistic ability to regiospecifically convert an α -halosulfone into an alkene. where the position of the newly formed double-bond is in no doubt. This is illustrated by the conversion of 5 into 6 upon reaction with aqueous sodium hydroxide. The main features of the mechanism are also summarized in this conversion. The bicyclic sulfone 7 is able to support through the pyramidal non-conjugative nature of the α -sulfonylcarbanion, a bridge-head carbanion which undergoes 1,3-elimination to the episulfone 8, subsequently extruding sulfur dioxide forming 9. Extremely strained propellanes are available via this type of rear-rangement.¹² A fascinating so-called bis-homoconjugative version of the Ramberg-Bäcklund reaction converts the α -chlorosulfone 10 into the cyclooctatriene derivative 11.13 Analogously a vinylogous equivalent of the Ramberg-Bäcklund reaction converts cis- or trans-3-bromo-2-pentenylbenzylsulfones into 1-phenyl-2-methyl-1,3pentadiene.14

Whilst the postulated episulfone intermediates in the Ramberg-Bäcklund reaction have not been isolated from a Ramberg-Bäcklund reaction, they have been prepared by other methods.¹⁵ Their decomposition to alkenes is base catalyzed which accounts for the inability to isolate them from a Ramberg-Bäcklund reaction. It has been observed that cis- and trans-2.3-diphenvlthiirane-1.1dioxide, 12 and 13 respectively, undergo stereospecific decomposition to the corresponding stilbenes. The Woodward-Hoffmann rules exclude a concerted thermal decomposition of thiirane-1,1-dioxides to alkenes, and consequently a dipolar mechanism has been suggested¹⁶ (Scheme 1). There seems to be no reason why thiirane-1,1-dioxides cannot rearrange either concertedly or via a short lived dipolar intermediate to a β -sultine 14. A β -sultine would be expected to readily extrude sulfur dioxide to give an alkene.¹⁷ The rearrangement of a thiirane-1,1-dioxide to a β -sultine has analogy in the chemistry of thiet-1,1-dioxides which readily rearrange to γ -sultines.¹⁷ The reaction of a diene with sulfur dioxide initially produces a sultine which rearranges to a sulfone. Attempted synthesis of the sultine resulted in the spontaneous loss of sulfur dioxide to give a diene, whereas the isomeric sulfone is quite stable under these conditions;18 although a Woodward-Hoffmann treatment of the chelotropic extrusion of sulfur dioxide predicts a disrotatory thermal fragmentation.¹⁹ These concepts are presented in Scheme 1. A recent observation that demonstrates that the mechanism of the Ramberg-Bäcklund reaction is by no means solved, is the suggestion that the rearrangement of 15 into 16 involves free-radicals.³



Download English Version:

https://daneshyari.com/en/article/5253602

Download Persian Version:

https://daneshyari.com/article/5253602

Daneshyari.com