

University of Groningen

α -Nitro sulfones and derivatives

Zeilstra, Jacobus Johannes

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version

Publisher's PDF, also known as Version of record

Publication date:

1975

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Zeilstra, J. J. (1975). *α -Nitro sulfones and derivatives: Chemistry and spectroscopy*. s.n.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

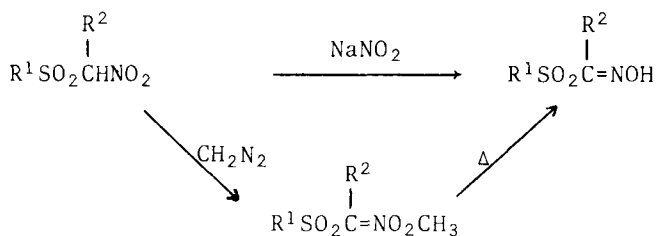
The work described in this thesis originates from our interest in sulfones with strongly electronegative α -substituents, *in casu* α -nitro sulfones ($R^1SO_2CR^2R^3NO_2$).

Chapter 1 contains an introduction and a survey of the literature. In addition, a short description is given of some important features, which are relevant for our investigations, of sulfones and nitroalkanes.

In *chapter 2* a new and facile synthesis of α -nitro sulfones is presented. This synthesis involves a reaction of *p*-tolylsulfonyl iodide with metal nitronates. The reaction is a free radical chain process rather than a nucleophilic displacement of iodide anion by the nitronate anion. A likely reaction path involves the intermediacy of α -iodo nitroalkane anion radicals. The synthetic procedure could be simplified by adding iodine to a solution of sodium *p*-toluenesulfinate and the appropriate potassium nitronate. In addition, electron transfer reactions to some α -nitro sulfones and the fate of the resulting anion radicals are described.

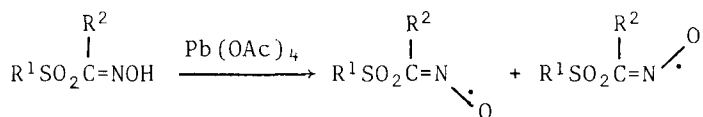
Chapter 3 deals with an investigation of the reactivity of α -nitro sulfones, bearing an α -H atom, in reactions like the Mannich condensation, the Michael addition and related condensations, *e.g.*, the condensation reaction of *p*-tolylsulfonynitromethane with aldehydes and benzenesulfinic acid. A proposed rationalization of the latter reaction involves the intermediacy of a nitro-olefin.

The syntheses of α -oximino sulfones from α -nitro sulfones are described in *chapter 4 and 6*.



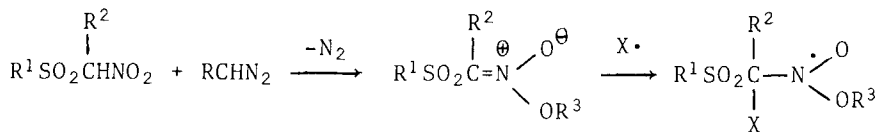
Upon reaction of these α -oximino sulfones with phosphorus pentachloride a Beckmann fragmentation was observed in addition to the well-known Beckmann rearrangement. This result is shortly discussed in *chapter 4*.

Chapter 5 deals with an esr spectroscopic study of α -sulfonyl iminoxy radicals. These (*syn*- and *anti*-) α -sulfonyl iminoxy radicals have been generated *in situ* by lead tetraacetate oxidation of α -oximino sulfones.



The esr spectra of the geometrical isomers have been assigned and the nitrogen and hydrogen hyperfine splitting constants are discussed in terms of the proposed structures. Evidence for some π -character of these σ -radicals is presented.

In *chapter 6* we report the isolation of five arylsulfonyl-alkanenitronic acid esters upon reaction of α -nitro sulfones, bearing an α -H atom, with diazoalkanes. Four of these esters readily add a variety of radicals to produce arylsulfonylalkyl alkoxy nitroxides which were studied by esr spectroscopy.



If the trapped radical is bulky, two nitrogen hyperfine splitting constants are observed. We infer that these nitroxides occur in two favoured conformations, both with the α -carbon to sulfonyl bond eclipsed with the half-filled orbital on nitrogen. The same types of nitroxides could also be generated by reaction of α -nitro sulfones with alkoxy carbonyl radicals. When the α -nitro sulfone contains a chiral center and the groups attached to the carbonyl radical site are different from each other, diastereomeric nitroxides are formed.

The dependence of the nitrogen hyperfine splitting constant on the substitution pattern in the nitroxides is discussed. The reaction of several nitronic acid esters with lead tetraacetate led to the production of α -sulfonyl iminoxy radicals. This reaction most likely proceeds *via* thermal decomposition into α -oximino sulfones and subsequent oxidation.

Finally, the *appendix* deals with the fragmentation pattern of some α -nitro sulfones under condition of electron impact. In many cases one of the fragments of the parent ion appears to be the *p*-toluenesulfonic acid radical cation.