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NEW DEAMINATIONS IX[1] - PYROLYSIS OF N-ALKYL-N,N-DISULFONIMIDES

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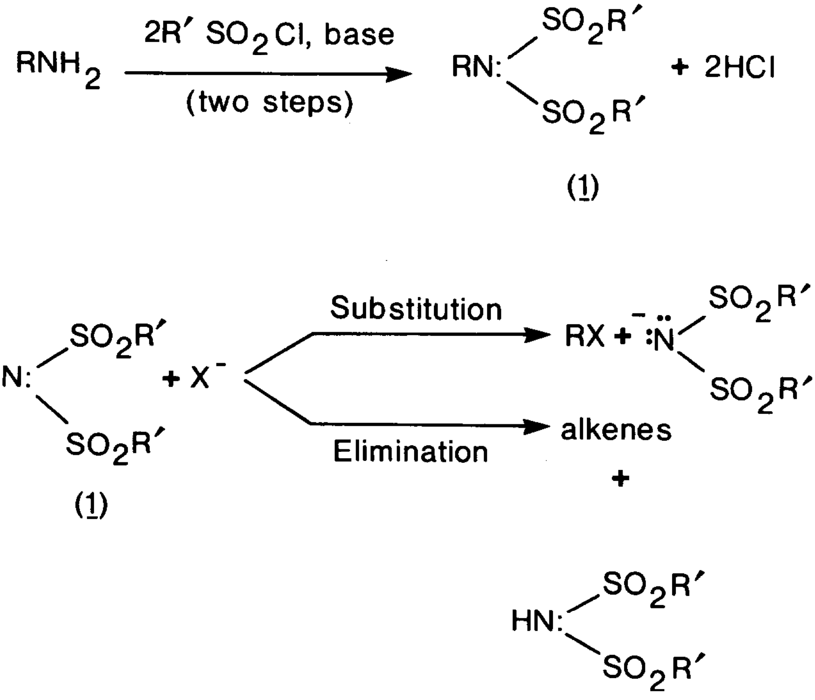
Abstract: N,N-Disulfonimide derivatives of certain alkyl amines stereoselectively pyrolyze without skeletal rearrangement to give up to 99% yields of alkenes.

N-Alkyl-N,N-disulfonimides (1) have been the subject of much recent deamination research due to the ease by which they are prepared from the parent amines and the facility by which they subsequently undergo substitution and/or elimination in the presence of a variety of nucleophiles (Eq.1).[1-13, 22, 23, 25] In most of the previous investigations the elimination reactions have been regarded as bothersome side reactions. Most commonly the yields of these alkenes have been low, but in cases such as those wherein the disulfonimide (1) is derived from a tertiary carbinamine, in the phenylethyl derivative of saccharin and other special cases; the alkenes are important or even the sole deamination products.[3, 4, 11-13]

Eq. 1



Sometimes, however, alkene formation is the desired pathway in synthesis. Thus, it would be useful to develop a set of conditions which would favor elimination with a greater variety of disulfonimides. Towards this end, we have previously attempted such devices as the use of stronger and bulkier bases. These methods have failed as the bases preferentially attacked the sulfur, resulting in sulfur-nitrogen bond cleavage.[12, 3]

Since a variety of functional groups such as the carboxylate ester, xanthate ester, amine oxide and amide groups can be pyrolyzed to give alkenes,[13-21] we recently decided to investigate whether disulfonimides (1) would thermally decompose to give alkenes.

We wish to presently report that N-alkyl-N,N-di(p-nitrobenzene)sulfonimide (2) derived from secondary carbinamines undergo elimination when they are heated in the absence of solvent at temperatures of ca. 160-200°C (Eq. 2). The yields of the corresponding alkenes range from 85 to 99% while the yields of the disulfonimide leaving group (3) are nearly quantitative. Our results are summarized in the table below. Alkene yields were probably higher than indicated, but significant amounts were lost in the runs due to the volatility of some of the alkenes.

Eq. 2

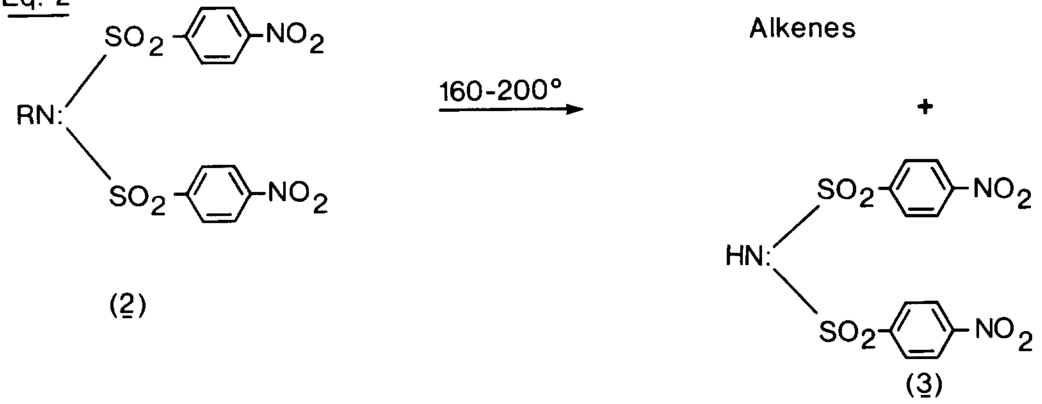


Table 1. Neat Pyrolyses of N-Alkyl-N,N-Disulfonimides

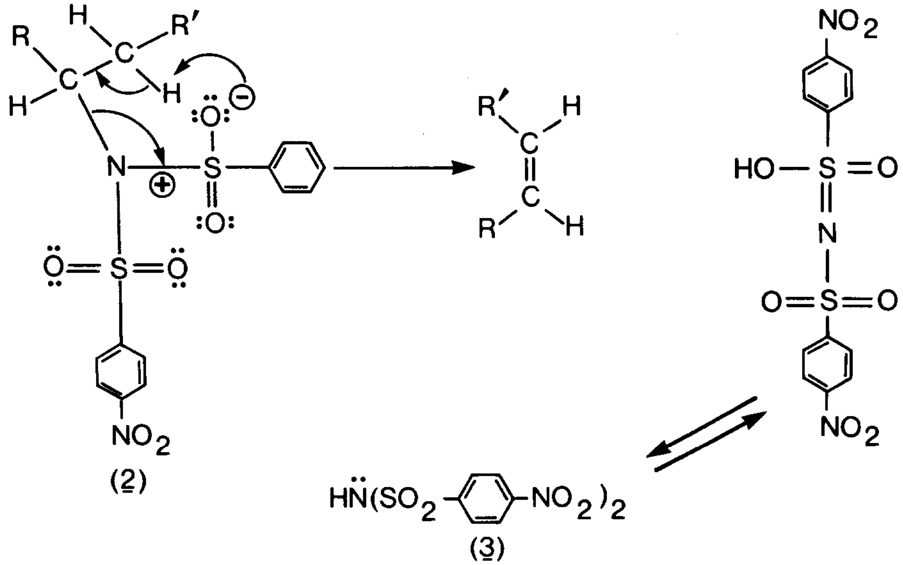
R group	Temp.	Time	Products*
Cyclooctyl	175°C	30 min	91% cis-cyclooctene, 99.8% $HN(Ns)_2$
Cyclodododecyl	180°C	30 min	86% cyclododecene
Cyclopentyl	175°C	30 min	90% cyclopentene, 95% $H-N(Ns)_2$
2-octyl	160°C	30 min	85% octene (mixture), 96% $H-N(Ns)_2$
2-phenylethyl	260°C	2 hrs	only starting material, no olefinic products
1-tetradecyl	260°C	2 hrs	only starting material, no olefinic products
1,2-diphenyl-ethyl	200°C	25 min	99% trans-stilbene (m. pt. 126-127°)

*IR, NMR, VPC, MP served to characterize products.

Disulfonimides (2) were prepared using the method described in paper V of this series.[4] Typically 0.50 g of the disulfonimide (2) was heated in a small round bottom flask over an oil bath heated to a temperature slightly above the decomposition temperature. A vacuum attachment served to transfer all alkene formed into a dry ice-acetone cooled receiver. The compound was heated until the boiling stopped, with usually 30 minutes being required to complete the reaction. Samples of disulfonimides (2) derived from primary carbinamines were heated to 160° to 300°C, but only starting material was isolated. The failure of the disulfonimide (2) derived from primary carbinamines to pyrolyze was not too surprising since it has been reported that xanthates and amides derived from the corresponding primary alcohols and primary carbinamines undergo pyrolytic decomposition to alkenes with great difficulty if at all.[15, 18, 19]

A plausible mechanism based on the analogy to the mechanism for the pyrolyses of esters, xanthates, and amine oxides is given in Eq. 3.[14-16]

Eq. 3



The complete stereoselectivity observed in the products from the pyrolysis of the cyclooctyl and 1,2-diphenylethyl derivatives, as well as the absence of any rearrangement products in the 1,2-diphenyl case (or any case), are consistent with the above mechanism. By comparison, Cope, Pike, and Spencer have found that N,N-dimethylcyclooctylamine oxide gives on pyrolysis at 100-125°, a 90% yield of cis-cyclooctene, while N,N,N-trimethylcyclooctylammonium hydroxide gives when pyrolyzed an 89% yield of a mixture of cyclooctene isomers (60% trans and 40% cis).[24]

An important advantage gained in the current pyrolyses over some of the analogous previous pyrolyses to produce alkenes, is the relatively low temperature required for these pyrolyses. For example most esters require pyrolytic temperatures in excess of 400°C, and most amides require pyrolytic temperatures of over 500°C.[15, 18, 19] Furthermore in these days of rapidly fluctuating prices for such chemicals as silver salts and methyl iodide, this procedure possesses a distinct economic advantage over the Hofmann elimination.

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