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NEW DEAMINATIONS VI: OXIDATIVE DEAMINATION - THE CONVERSION OF SECONDARY CARBINAMINES INTO KETONES

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It has previously been discussed and reported in papers in this series[1-5] and elsewhere[6-9], that N-alkyl, N,N-disulfonimides (1) often behave analogously to alkyl sulfonates (2) (Eq. 1 and 2). Since the disulfonimides (1) may be prepared almost as readily as the corresponding sulfonates (2),[1-3,5] many of the reactions of these disulfonimides (1), serve as convenient new deamination procedures (Eq. 2).[1-5]

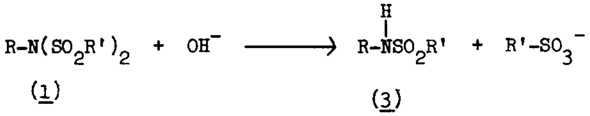
$$RN(SO_2R')_2 \quad (1) \qquad\qquad R{-}OSO_2R' \quad (2)$$

Eq. 1 $$ROSO_2R' + X^- \xrightarrow{DMF} RX + R'SO_3^- + HCl$$

Eq. 2 $$RN(SO_2R')_2 + X^- \xrightarrow{DMF} RX + {}^-{:}\ddot{N}(SO_2R')_2$$

But not all the reactions of the N-alkyl-N,N-disulfonimides (1) are analogous to the reactions of the corresponding sulfonates (2). For example, when X^- (Eq. 2) is a nucleophile such as hydroxide, cyanide, or mercaptide; sulfur-nitrogen bond cleavage occurs preferentially to carbon-nitrogen bond cleavage (Eq. 3).[5,10,11]

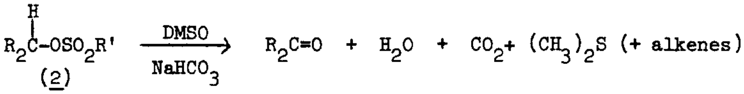
Eq. 3



$$\underset{(1)}{R{-}N(SO_2R')_2} + OH^- \longrightarrow \underset{(3)}{R{-}\overset{H}{\overset{|}{N}}SO_2R'} + R'{-}SO_3^-$$

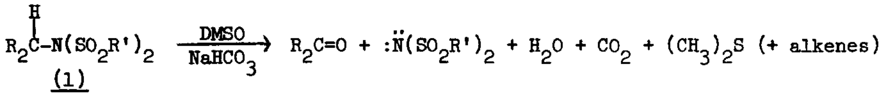
In any case, none of the previously reported deaminations of (1) were of the oxidative deamination type. These are illustrated here using the known oxidations of (2) as a model analogy (Eq. 4a and 4b):

Eq. 4a: Conversions of alkyl sulfonates (2) into carbonyl compounds via oxidation with dimethyl sulfoxide (DMSO) and sodium bicarbonate[12,13]:



$$\underset{(2)}{R_2\overset{H}{\overset{|}{C}}{-}OSO_2R'} \xrightarrow[NaHCO_3]{DMSO} R_2C{=}O + H_2O + CO_2 + (CH_3)_2S \text{ (+ alkenes)}$$

Eq. 4b: The proposed conversions of disulfonimides (1) into carbonyl compounds via oxidation with dimethyl sulfoxide and sodium bicarbonate:



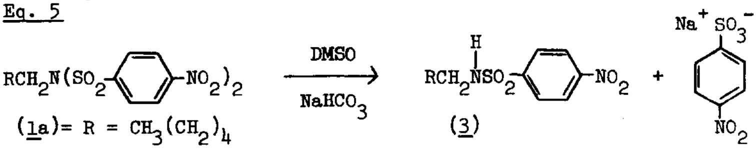
$$R_2\overset{H}{C}\text{-}N(SO_2R')_2 \xrightarrow[NaHCO_3]{DMSO} R_2C{=}O + :\ddot{N}(SO_2R')_2 + H_2O + CO_2 + (CH_3)_2S \text{ (+ alkenes)}$$

(1)

This paper reports our findings in relation to the oxidative deaminations outlined in Eq. 4b. The analogous oxidations of sulfonate esters (2) (Eq. 4a) have been well documented.[12,13]

Interestingly, we found that both C-N and S-N bond cleavage occur. In particular, for primary carbinamines (1a), only sulfur-nitrogen bond cleavage (Eq. 5) has been so far observed, while for secondary carbinamines the desired oxidative carbon-nitrogen bond cleaveage occurs (Eq. 6).

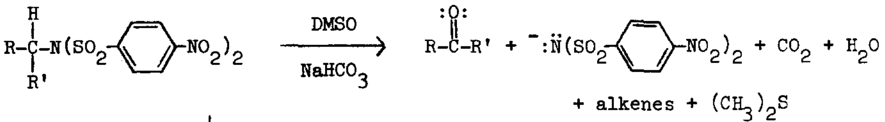
Eq. 5

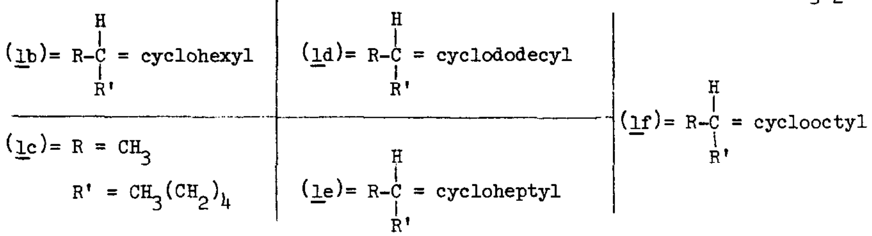


(1a)= R = $CH_3(CH_2)_4$

(3)

Eq. 6





(1b)= R-C-R' = cyclohexyl

(1c)= R = CH_3

R' = $CH_3(CH_2)_4$

(1d)= R-C-R' = cyclododecyl

(1e)= R-C-R' = cycloheptyl

(1f)= R-C-R' = cyclooctyl

Our results are summarized in the following table:

Disulfonimide (1)	% Yield of Ketone	% Yield of Alkene	% Yield of Sulfonamide(3)
(1 a)	-	-	58
(1 b)	67	*	-
(1 c)	60	*	-
(1 d) 159-160°†	5	88	-
(1 e) 183° (decomp)†	58	22	-
(1 f) 160° (decomp)†	37	36	-

* Not searched for

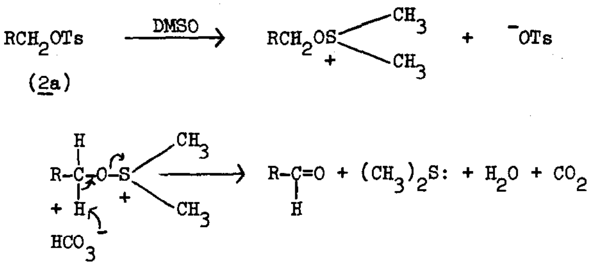
† Melting points are reported for new compounds

Typically, 2.1 mmoles of (1a-f) (prepared as described in our previous paper[1]) were heated with 60 mmoles of sodium bicarbonate in 20 cc. of DMSO at 100° for 12-48 hrs. The ketonic and alkene products were qualitatively and quantitatively identified with the aid of NMR and IR, 2,4-DNP, vpc, and column chromatography.

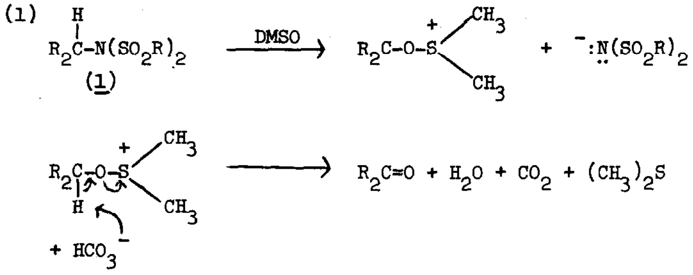
The exceptionally high proportion of alkene to ketone obtained with (1d) was not unexpected based on previous studies which indicated that SN type reactions occur with great difficulty in these systems[14,15]. However, the best ketone yields were obtained with the cyclohexyl case, and this is indeed surprising.

A possible mechanism for the oxidations in Eq. 6 would be one which is analogous to the proposed mechanisms for the corresponding oxidation of tosylates (2a)[12] (Schemes I and II).

Scheme I: The Proposed Mechanism of Oxidation of Tosylates (2a):[12]



Scheme II: The Currently Proposed Mechanism for the Oxidation of Disulfonimides:



Bosworth and Magnus, however, have obtained some evidence in certain cases for an alternate oxidation mechanism wherein the bicarbonate ion may act as a nucleophile.[13]

There is not, at present, enough evidence to distinguish between SN^1 and SN^2 in the first step of the currently proposed mechanism. Experiments are in progress to distinguish between these two pathways.[16]

Other types of oxidative deamination have been reviewed.[4,6] Most of these procedures involve direct oxidations of the parent amines with variable yields.

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References and Notes

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