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SIMPLE DEAMINATIONS VIII[1] - NEW APPROACHES TO THE CONVERSION OF THE CARBON-NITROGEN BOND TO THE CARBON-OXYGEN BOND

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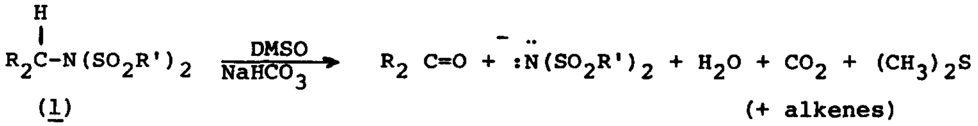
In previous papers in this series[1-5], as well as in other publications[6-10], various results have been reported to illustrate that N-alkyl-N,N-disulfonimides (1) behave similarly to alkyl sulfonates (2) (Eq. 1 and 2). Since the disulfonimides (1) are readily obtained in excellent yields[3,10], these disulfonimides (1) can be used for various deaminations (Eq. 1).[1-8]

Eq. 1 $$\underset{(\underline{1})}{R\text{-}N(SO_2R')_2} + X^- \xrightarrow{DMF} RX + :\overset{-\,\cdot\cdot}{N}(SO_2R')_2$$

Eq. 2 $$\underset{(\underline{2})}{R\text{-}OSO_2R'} + X^- \xrightarrow{DMF} RX + R'SO_3^-$$

However, as has been noted in the previous papers in this series,[1-5] the very important conversion of the carbon-nitrogen bond to the carbon-oxygen bond has met with some problems. In particular, the reaction of (1) with the hydroxide anion, results in sulfur-nitrogen rather than carbon-nitrogen bond cleavage.[2,4] This behavior led to our previous studies which used indirect methods to deaminate the imides (1) to oxygen derivatives.[1,2] One of these approaches involved oxidative deamination to form ketones (Eq. 3).[2] The formation of aldehydes has, however, so far only been observed for the benzylamine derivative, and then only in very low yield.[2]

Eq. 3 

$$\underset{(\underline{1})}{R_2\overset{\overset{\displaystyle H}{|}}{C}\text{-}N(SO_2R')_2} \xrightarrow[NaHCO_3]{DMSO} R_2\,C{=}O + :\overset{-\,\cdot\cdot}{N}(SO_2R')_2 + H_2O + CO_2 + \underset{(+\text{ alkenes})}{(CH_3)_2S}$$

The second previous approach for deamination to form carbon-oxygen bonds from (1), involved the use of the strong acid HI in DMF to give alcohols and formate esters[1] (Eq. 4). The main disadvantage to this method was the necessity for strongly acidic conditions; thus, any polyfunctional compounds with acid labile groups would be vulnerable to complications under these acidic conditions.

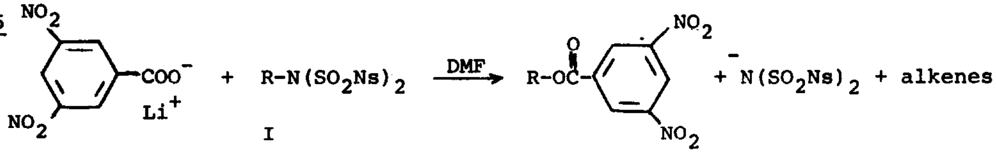
Eq. 4 $R\text{-}N(SO_2R')_2 + HI + HCON(CH_3)_2 + H_2O \longrightarrow R\text{-}OOCH + ROH$

(1)

We wish to now discuss two new approaches in respect to deaminations of (1) to form alcohols or alcohol derivatives which involve neither oxidation nor acidic conditions.

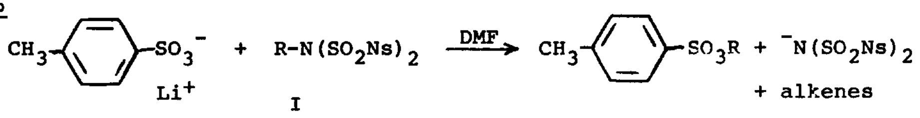
The first of these approaches involves the conversion of the dinosylsulfonimide I to 3,5-dinitrobenzoate esters via nucleophilic displacements by the 3,5-dinitrobenzoate anion (Eq. 5).

Eq. 5



The second of these approaches involves the conversion of I to the tosylate ester (Eq. 6).

Eq. 6



Typical results from the above two approaches are given in Tables A and B.

Table A: Reactions of Lithium 3,5-Dinitrobenzoate with $R\text{-}N\begin{smallmatrix}Ns\\Ns\end{smallmatrix}$ I B.

(All runs were done in at least duplicate)

R group	Temp & Solvent	Time	Conc. of imide I (M)	Molar excess of Lithium 3,5-dinitrobenzoate	Product(s)
n-Hexyl	140°C in DMF	24 hrs	.085	1.15	57% n-hexyl 3,5-dinitrobenzoate
n-Dodecyl	140° in DMF	24 hrs	.072	1.1	60% n-dodecyl 3,5-dinitrobenzoate
Cyclohexyl	107° in DMF	24 hrs	.066	1.3	60% cyclohexene 12% cyclohexyl 3,5-dinitrobenzoate
Cyclohexyl	100° in DMSO	24 hrs	.105	2	72% cyclohexene 3% cyclohexyl 3,5-dinitrobenzoate
Cyclododecyl	100° in DMSO	24 hrs	.05	2	55% cyclododecene 3.5% cyclodecyl 3,5-dinitrobenzoate

Table B

Reactions of Lithium Tosylate with $R\text{-}N{<}^{Ns}_{Ns}$ I

(All runs were done in at least duplicate)

R group	Solvent & Temp	Time	Conc. of imide I (M)	Molar excess of nucleophile	Products
n-hexyl	DMF 152° (reflux)	1 hr	.275	10	18.5% n-hexyl tosylate 50% starting material I
n-dodecyl	DMF reflux	18 hrs	.128	10	23% n-dodecanol 57% n-dodecyl formate
2-octyl	DMF reflux	18 hrs	0.1	10	22% 2-octyl formate
benzyl	DMF reflux	18 hrs	.175	10	70% benzyl formate
2-phenyl-ethyl	DMF reflux	24 hrs	0.100	10	43.3% 2-phenyl-ethyl formate

A typical run with lithium 3,5-dinitrobenzoate involved heating a 2 Molar excess of lithium 3,5-dinitrobenzoate with disulfonimide I at 100 to 140° in dry DMF for 24 hrs. The products were extracted with ether (or methylene chloride or hexane), washed with bicarbonate and H_2O and purified by column chromatography. The 3,5-dinitrobenzoate esters were identified via NMR, IR, and mixed m. pts. with known samples.

A typical run with lithium tosylate involved refluxing I with a 10M excess of lithium tosylate in dry DMF for 24 hours. The products were isolated with ether or CH_2Cl_2, and washed with sodium bicarbonate solutions and water. Column chromatography was used for separations while NMR, IR, and m. pts. were used for identification.

It was not especially surprising to find formate esters as important products in the tosylate runs, since we had previously observed such esters during the reactions of 1 with HI.[1] The question arose, however, as to how the ester formed. In particular it is most likely that the tosylate anion first displaces the disulfonimide leaving group, followed by a SN of the tosylate anion by the formate anion. The question next arises as to the origin of the formate anion. The probable answer is that since the tosylate anion is a weak base, it is catalyzing the decomposition of the DMF to formate ion and dimethylamine. The instability of DMF in acids and bases has been previously observed.[1,11] In fact there is even some conversion of dodecyl I to formate ester after 20 hrs. in DMF (34% I and 42% formate ester). Since n-hexyl tosylate has been isolated, and since no I remains after 18 hrs. reflux in any of our runs with tosylate, it is probable that at least some of the yield of C-O products occurs via prior tosylate formation. When n-hexyl tosylate was refluxed alone in DMF for 20 hrs, mostly alkene; and 3% starting material were observed. Thus, it would appear that a catalyst such as tosylate anion is necessary for formate formation.

Other methods for the conversion of amines to alcohols and their derivatives such as the nitrous acid, the nitrosoamide, the triazene, and the diazotate techniques are, of course, well known.[12-17]

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