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A NOVEL DEAMINATION:
THE SYNTHESIS OF STYRENE FROM 2-PHENYLETHYL AMINE VIA THE UTILIZATION OF THE SACCHARIN ANION AS A LEAVING GROUP.

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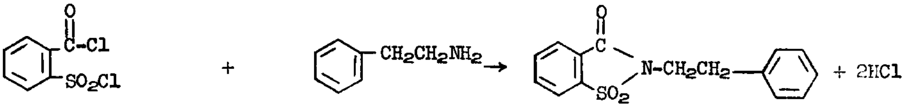
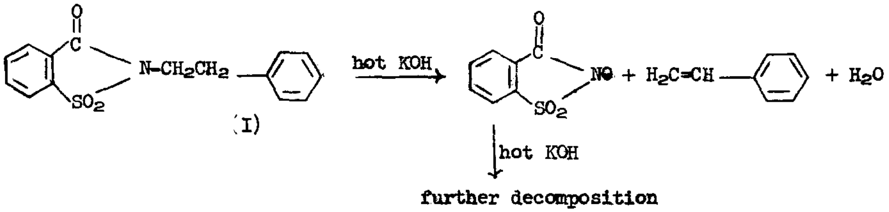
Dehydroxylations are commonly accomplished via nucleophillic substitutions and eliminations on derivatives such as the tosyl esters of the parent alcohols. Groups such as the tosylate anion are presumably much better leaving groups than the hydroxide anion, mainly because of the relatively weakly basic nature of the tosylate anion.

As predicted by the present author in a recent review article (3), analogous deaminations, utilizing sulfonimide type derivatives of amines, should be observable in at least some cases. We wish to report a successful example of such a deamination procedure. Specifically, styrene is produced in 65% yield upon the heating of N-2-phenylethyl saccharin (I) with potassium hydroxide (scheme 1):

Scheme 1:



(I)



When the saccharin derivative I, prepared by the method of Rice and Pettit (4) (5) (m.p. 138-139°; lit. (4). m.p. 138-139°; infrared spectrum, nuclear magnetic resonance spectrum and elemental analyses all consistent with the N-alkylated derivative I) was heated with a four-fold molar excess of potassium hydroxide pellets over a micro-Bunsen burner in a micro-distillation apparatus at 50-100 mm, crude styrene and water distilled. A heating time of about five minutes was necessary. The crude volatile product gave a 65% yield of styrene (whose infrared and nuclear magnetic spectra were identical with the corresponding spectra of authentic styrene) after appropriate drying and redistillation. No 2-phenylethanol was detected on a thin layer plate of the crude product. Styrene was not obtained when the N-alkyl derivative (II) was heated without base.

The 65% yield of styrene obtained by the presently described method compares favorably with the 38-41% yields reported in "Organic Synthesis" for the synthesis of styrene from cinnamic acid or with the 31-82% yields of substituted styrenes obtained via the dehydration of alcohols (6) (7). The yields of various styrenes prepared from phenylethyl amines via the Hofmann elimination procedure range from 25-100% (8) (9). The Hofmann elimination, however, is a relatively time-consuming and expensive process. Moreover, preliminary results indicate that styrene may be obtainable in good yields from the especially easy to synthesize N-2-phenylethyl phthalimide derivative.

The various other techniques available for the synthesis of styrene and substituted styrenes have been reviewed (9) (10).

The absence of any products derived from nucleophillic substitution was not particularly surprising, since many cases have been observed with Hofmann eliminations, wherein only alkene formation or almost exclusively alkene formation occurs (8).

The production of small amounts of ethyl acrylate when N-2-carbethoxyethyl saccharin is heated with potassium hydroxide, suggests that this type of deamination may occur with other amines capable of yielding conjugated alkenes.

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References

1. To whom inquiries regarding this communication should be addressed. After September 1st, please address all inquiries to the Chicago Circle Campus.
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