Trapping an Intermediate with Styrene and 2-Phenylbicyclo[2.2.1]hept-2-ene in the Polonovski Demethylation Reaction

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The products of the demethylation of tertiary amine *N*-oxides containing at least one *N*-methyl group are *N*-acetylated secondary amines and formaldehyde (the Polonovski demethylation reaction). A free radical^{1,2} or an ylide³ mechanism has, in some reports, been proposed for this reaction. However, in most publications⁴ an iminium ion is assumed to be the actual intermediate.

Styrene has been used in the mechanistical studies of the Polonovski reaction. Huisgen *et al.*⁵ rejected the free radical mechanism when they did not observe polymerization under reaction conditions at –10–0°C. In turn, Hayashi *et al.*³

proposed the ylide mechanism on the basis of the formation of benzyl acrolein (1) and *N*-acetylated benzenepropanamine (2) in the Polonovski reaction of trimethylamine *N*-oxide in the presence of styrene.

The amide 2 formed under the Polonovski reaction conditions is clearly an acetylation product of the secondary amine 3, which is also one of the major products in the aminomethylation of styrene.⁶ The other principal aminomethylation products of styrene are aldehyde 1 and amine 4, as we have recently shown.⁷ The initial intermediate of the aminomethylation is the *N,N*-dimethylmethyleniminium ion (5), from which

Scheme 1.

compounds **1**, **3** and **4** are formed as a result of hydride transfer from the *N*-methyl carbon of **5** to the α carbon of styrene, and via the subsequent reactions presented in Scheme 1. The finding that **1**, **3** and **4** are the major products in the aminomethylation of styrene led us to repeat the Polonovski demethylation reaction of trimethylamine *N*-oxide in the presence of styrene as described by Hayashi *et al.*³

Styrene (0.025 mol), dried⁸ trimethylamine *N*-oxide (0.05 mol) and acetic anhydride (0.1 mol) were heated in chloroform (60 ml) for 5 h. The major components derived from styrene in the crude product mixture, with a yield of 4.0 g, containing also unreacted styrene, were aldehyde **1** and amide **2** as reported earlier³ plus the amide **9**, which is the *N* acetylation product of **4**. The analytical data of **1** and **2** were as reported.³ The identification of **9** was based on the comparison of mass and ¹³C NMR spectra with those of an authentic sample obtained from **4**.⁷ Two minor components in the product mixture were identified as *N,N*-dimethylbenzenepropanamine (**10**) and *N*-methyl-*N*-(3-phenylpropyl)benzenepropanamine (**11**), which are *N* methylation products of **3** and

4, respectively. Compounds **10** and **11** were identified by mass spectral comparison with authentic samples.⁷

To compare further the intermediate in the aminomethylation of an alkene with that of the Polonovski demethylation reaction, trimethylamine *N*-oxide was allowed to decompose in the presence of 2-phenylbicyclo[2.2.1]hept-2-ene (**12**), which was easily aminomethylated with the iminium ion **5**.⁹ The products derived from **12** were aldehyde **13**, acetylated secondary amines **14** and **15**, amino acetate **16** and the tertiary amine **17**. In the aminomethylation of **12**,⁹ the compounds formed were **13**, the secondary amines **18** and **19**, which are precursors of **14** and **15**, respectively, the amino alcohol **20**, which is a precursor of **16**, and **17**. The identification of **13**, **14**, **15**, **16** and **17** formed under the Polonovski reaction conditions was based on mass spectral comparisons with the compounds synthesized during the aminomethylation of **12**.

Our present trapping experiments with styrene and 2-phenylbicyclo[2.2.1]hept-2-ene (**12**) show that the same products are formed from these compounds in the Polonovski demethylation reaction as in the aminomethylation reaction.^{6,9} Therefore, there is no need to explain the Polonovski demethylation of trimethylamine *N*-oxide by the ylide mechanism. The mechanism whereby **5** is formed, as presented by Huisgen *et al.*,⁵ and continues to react, as shown in Scheme 1, is reasonable for the formation of the aldehydes and the amines under the Polonovski reaction conditions when alkenes like styrene or **12** are present.

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