Arylamines as Leaving Groups in Elimination Reactions

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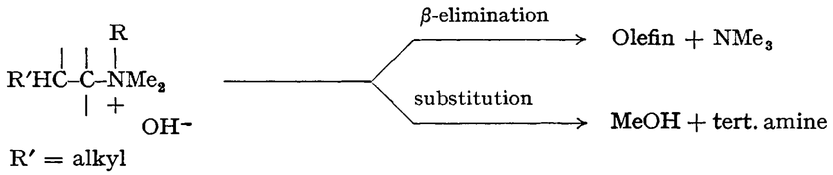
WHILE investigating Hofmann decomposition of quaternary ammonium hydroxides, Archer and Booth[1] observed that although β-elimination is the predominant pathway starting with an alkyltrimethylammonium hydroxide (R = Me), the alternative substitution or displacement process (giving methanol and tertiary amine) is preferred when an alkyldimethylphenylammonium hydroxide (R = Ph) is decomposed.

In an earlier study, Burrows and Eastman,[2] commenting on the large amount of substitution which took place during degradation of a cyclic arylammonium compound, the tetrahydrodimethylquinolinium hydroxide (I), suggested that "the electron-rich, highly polarizable group attached to the quaternary nitrogen may so diffuse the positive pole on the nitrogen as to reduce the acidity of the proton on the β-carbon below the level required for elimination".

In terms of ratios of rate constants, the Hofmann



results can be described by the inequality $k_\beta^{\mathrm{Me}}/k_{\mathrm{sub}}^{\mathrm{Me}} > k_\beta^{\mathrm{Ph}}/k_{\mathrm{sub}}^{\mathrm{Ph}}$ where the superscript represents the R group and the subscript the type of reaction. Thus the explanation given above suggests that $k_\beta^{\mathrm{Me}} > k_\beta^{\mathrm{Ph}}$ while presumably $k_{\mathrm{sub}}^{\mathrm{Me}} \approx k_{\mathrm{sub}}^{\mathrm{Ph}}$.

In the light of these observations concerning *E*2 and S_N2 competition and because of our interest in competitive β- and γ-elimination reactions of 3-phenylpropyl derivatives,[3] we studied the decomposition of 3-phenylpropyltrimethylammonium methosulphate (II) and 3-phenylpropyldimethylphenylammonium methosulphate (III) with potassium t-butoxide in dimethyl sulphoxide. This combination permitted the study to be conducted under homogeneous conditions.

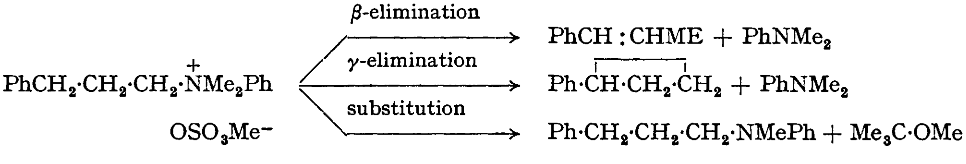
Treatment of (II) with an equimolar amount of base for 3 hr. at 100° gave 1-phenylpropene (85%). This olefin undoubtedly arises *via* base-catalyzed isomerization of the initially formed 3-phenylpropene.[4]

$$\mathrm{PhCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}Me_3\quad OSO_3Me^-} \xrightarrow{\beta\text{-elimination}} [\mathrm{PhCH_2{\cdot}CH{=}CH_2}] \longrightarrow \mathrm{PhCH{:}CHMe}$$

(II)

No other hydrocarbon products were detected so β-elimination represents the exclusive pathway in this case.

Similar treatment of (III), however, yielded (80%) products resulting from β-elimination, γ-elimination, and substitution in a molar ratio of 2·5 : 1·0 : 1·6, respectively according to gas-phase chromatography and n.m.r. analyses.



(III)

Therefore in comparing (II), which has an aliphatic amine as leaving group, with (III), which has an aromatic amine, the same trend appears as noted in the Hofmann series, namely that $k_\beta^{\mathrm{Me'}}/k_{\mathrm{sub}}^{\mathrm{Me'}} > k_\beta^{\mathrm{Ph'}}/k_{\mathrm{sub}}^{\mathrm{Ph'}}$ where Me′ refers to (II) and Ph′ to (III). Also, comparison of β-elimination and γ-elimination, an internal displacement process, reveals a similar inequality $k_\beta^{\mathrm{Me'}}/k_\gamma^{\mathrm{Me'}} > k_\beta^{\mathrm{Ph'}}/k_\gamma^{\mathrm{Ph'}}$.

These results, in analogy with the Hofmann cases, could be obtained if $k_\beta^{\mathrm{Me'}} > k_\beta^{\mathrm{Ar'}}$ and $k_{\mathrm{sub}}^{\mathrm{Me'}} \approx k_{\mathrm{sub}}^{\mathrm{Ar'}}$ and $k_\gamma^{\mathrm{Me}} \approx k_\gamma^{\mathrm{Ar'}}$. Such an argument requires that $k_\beta^{\mathrm{Me'}} + k_{\mathrm{sub}}^{\mathrm{Me'}} + k_\gamma^{\mathrm{Me'}} > k_\beta^{\mathrm{Ar'}} + k_{\mathrm{sub}}^{\mathrm{Ar'}} + k_\gamma^{\mathrm{Ar'}}$.[5]

To compare the relative rates of reaction of (II) and (III), we exposed a mixture of these quaternary salts to an insufficient amount of base.† Compound (III) was consumed (at 100°), more rapidly than compound (II).

From the finding that $k_\beta^{\mathrm{Me'}} + k_{\mathrm{sub}}^{\mathrm{Me}} + k_\gamma^{\mathrm{Me}} < k_\beta^{\mathrm{Ar'}} + k_{\mathrm{sub}}^{\mathrm{Ar'}} + k_\gamma^{\mathrm{Ar'}}$ and the observations that $k_\beta^{\mathrm{Me'}}/k_{\mathrm{sub}}^{\mathrm{Me'}} > k_\beta^{\mathrm{Ar'}}/k_{\mathrm{sub}}^{\mathrm{Ar'}}$ and $k_\beta^{\mathrm{Me'}}/k_\gamma^{\mathrm{Me'}} > k_\beta^{\mathrm{Ar'}}/k_\gamma^{\mathrm{Ar'}}$ we conclude that the effect of changing the leaving group from an aliphatic amine to an aromatic amine (II→III) cannot be accounted for solely by differences in the numerators of the above ratios but must be influenced by differences in the denominator terms.

This could mean that replacement of an *N*-methyl group with an *N*-aryl group in a quaternary compound not only decreases the acidity of the β-hydrogen but makes the amine a better leaving group.

In the activated complex for substitution, some attachment of the nucleophile has occurred at the α-carbon atom while partial detachment of the amine has taken place. Therefore, the ability of an aromatic amine to act as an electron sink (by delocalizing the electrons being set free by the nucleophile's attack) will lower the energy of the transition state and make $k_{\mathrm{sub}}^{\mathrm{Ar'}} > k_{\mathrm{sub}}^{\mathrm{Me'}}$.‡

Although in the complex for β-elimination there is considerable β-H bond breaking, the C–N bond is still largely intact so less charge relative to the substitution case is transferred to the amine. Consequently the ability of the leaving group to

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† The reasonable assumption is made that these processes are all bimolecular. No reaction was observed when the butoxide was omitted.

‡ Statistically the larger number of methyl groups on (II) favours the S_N2 process.

stabilize negative charge makes less impact in β-elimination.

This analysis based on experiments with compounds (II) and (III) appears to be applicable to elimination reactions of quaternary ammonium salts generally.

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[4] C. L. Bumgardner, *J. Amer. Chem. Soc.*, 1961, **83**, 4423.