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ELECTROLYTIC GENERATION OF STRONG BASES.
II. STEVENS REARRANGEMENT[1]

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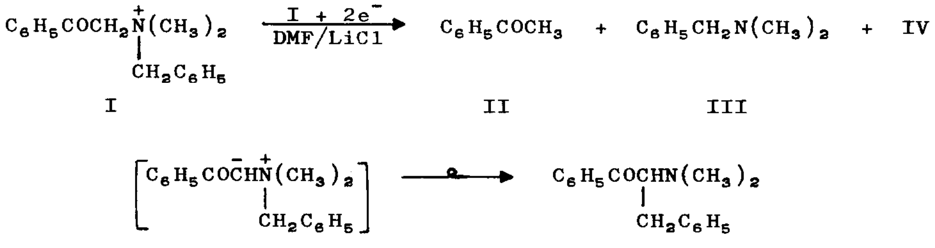
Recently it was demonstrated that electrolytically generated azobenzene anion could be used to induce the Wittig reaction[2]. Some other base-promoted reactions have since been investigated by this technique, and the possibility of performing a Stevens rearrangement has now been realized using benzyldimethylphenacylammonium bromide (I) as the substrate. In this case azobenzene could not be used as a depolarizer, because it is reduced at a potential about 0.2 V more negative than I in DMF. However, by using I both as the depolarizer and the substrate, the following reaction took place in the electrolytic cell:



$$\underset{\textbf{I}}{C_6H_5COCH_2\overset{+}{N}(CH_3)_2(CH_2C_6H_5)} \xrightarrow[DMF/LiCl]{I\ +\ 2e^-} \underset{\textbf{II}}{C_6H_5COCH_3} + \underset{\textbf{III}}{C_6H_5CH_2N(CH_3)_2} + IV$$

$$\underset{\textbf{IV}}{\left[C_6H_5CO\overset{-}{C}H\overset{+}{N}(CH_3)_2(CH_2C_6H_5)\right]} \xrightarrow{a} \underset{\textbf{V}}{C_6H_5COCH(CH_2C_6H_5)N(CH_3)_2}$$

Thus reduction of I (0.04 mole) on a mercury cathode at 85-90° in DMF/LiCl (20 g/l) at potentials above -0.8 V vs Ag/AgCl in a conventional 3-electrode H-type cell[3] consumed nearly 1 F/mole. Acetophenone (II) and benzyldimethylamine (III) could be detected (not estimated quantitatively) by GLC directly in the catholyte. II was isolated in 46% yield (max. 50% from I) by extraction with petrol ether after the addition of 25 ml of 4 N HCl and diluting the catholyte with the double volume of water. A mixture of the basic compounds III and IV was isolated by benzene extraction of the catholyte after making alkaline as a yellowish oil which solidified. Recrystallisation from a 3:2 methanol-water mixture (25 ml) gave 36% of pure V, identified as ω-benzyl- ω-dimethylaminoacetophenone by comparing its m.p. (78-79°), IR- and NMR-spectra (ABM-system) with those of an authentic specimen[4]. A control experiment of the work-up procedure showed 99% recovery of II and 91% of V (recryst.prod.); the stated yields of II and V have not been corrected for loss during the isolation.

The experiment is of course of no synthetic value for the preparation of V, but represents another case, where a substance can function as a proton donor for its own electrolytic reduction being the strongest acid present[5-7].

Electrolysis at 0-5° (ice cooling) gave practically the same amount of V. However, addition of water (1% or 5% by vol.) to the DMF caused a decrease to 15% and 23% of rearranged product, while the starting material was isolated as the fluoborate in 31% and 26%, respectively. Addition of an equimolar amount of a stronger[8], but less reducible acid like phenacyl- or carbethoxymethylene-triphenylphosphonium bromide increased the electron consumption to nearly 2 F/mole, and no V, only II and III were found. Addition of equimolar amounts of benzaldehyde and benzyltriphenylphosphonium bromide resulted in a Wittig reaction with very high yields (> 95% isolated) of cis-trans stilbene and triphenylphosphine oxide, while V could not be found in the basic extract.

Attempts to perform a Stevens rearrangement by reducing azobenzene in DMF in the presence of benzyltrimethyl- or dibenzyldimethylammonium bromide were unsuccessful. No rearranged products were found, meaning that the azobenzene anion is not sufficiently basic to abstract a proton forming the corresponding N-ylides.

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