Electrolytic Cleavage of β-Ketosulfoxides

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Corey and Chaykovsky [1,2] have described a general method for the transformation of an ester into the corresponding methyl ketone in two steps. First, the ester is condensed with sodium methylsulfinylmethide (generated from dimethyl sulfoxide and sodium hydride). In the second step, the β-ketosulfoxide thus formed is treated with aluminium amalgam causing the formation of ketone by reductive cleavage of a carbon-sulfur bond.

Both steps of the reaction sequence are essentially quantitative, but from a practical point of view, the handling of aluminium amalgam is rather awkward except in small-scale preparations. Another difficulty on scaling up the synthesis is the maintenance of a sufficiently short reaction time necessary for the preparation of aromatic ketones by this method.

Since aluminium amalgam can be considered to act as a short-circuited galvanic element, it was logical to investigate if the reductive cleavage leading to a methyl ketone could be brought about by electrolysis. Preliminary work has revealed that this process does indeed take place, and below, the syntheses of two representative ketones, 2-octanone and *p*-methoxyacetophenone will be described.

The electrolyses were performed at a mercury cathode, the potential of which was controlled with aid of a potentiostat. A platinum anode was used, and the anolyte and catholyte were separated by a sintered-glass diaphragm. In order to find the optimum conditions for the syntheses, a polarographic investigation of the β-ketosulfoxides used as precursors to the ketones had to be carried out. The details of this investigation will be reported later.

Experimental. Melting points were determined on a Kofler Heizbank. The identity of the final products was ascertained by comparison with authentic samples.

Methylsulfinylmethyl hexyl ketone was prepared from ethyl heptanoate and dimethyl sulfoxide according to Corey and Chaykovsky.[1,2] M.p. 58°.

Of this β-ketosulfoxide, 19 g (0.1 mole) was dissolved in 200 ml of 50% aqueous dimethylformamide containing 10 g of potassium nitrate as supporting electrolyte. In order to get an acceptable yield of 2-octanone, it was necessary to perform the electrolysis under a layer of pentane (100 ml) which served to extract the product as it was formed. Thorough mixing was ensured. During the run, the pentane was replaced ten times. The cathode potential *vs.* a saturated calomel electrode was −1.74 V. The catholyte was maintained at pH 11 by controlled addition of 2 M hydrochloric acid with an electrometric titrator. When the theoretical amount of current, 4 F/mole,* had been introduced, the catholyte was diluted with 300 ml of water, the mixture saturated with sodium chloride and extracted with pentane. The organic phase was combined with the ten portions of pentane obtained above, washed with water and dried. Distillation gave 6.9 g (54 %) of 2-octanone, b.p. 90°/40 mm.

ω-(Methylsulfinyl)-*p*-methoxyacetophenone was prepared from ethyl anisate and dimethyl sulfoxide as above.[1,2] The substance had a double m.p. at 97° and 103°; lit.[2] 96° and 104−105°.

The electrolysis was performed as above but without pentane, and the run was interrupted when 97 % of the theoretical amount of current had been introduced. Over-electrolysis caused the yield to decrease drastically. The cathode potential *vs.* a saturated calomel electrode was −1.60 V, pH of the catholyte 11. After extraction with ether and the usual work-up, 11 g (74 %) of *p*-methoxyacetophenone was obtained, b.p. 82°/0.7 mm.

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1. Corey, E. J. and Chaykovsky, M. *J. Am. Chem. Soc.* **86** (1964) 1639.
2. Corey, E. J. and Chaykovsky, M. *J. Am. Chem. Soc.* **87** (1965) 1345.

* The other reaction product is believed to be methyl mercaptan. Fortunately, the mercury cathode remains unaffected during the conditions of electrolysis.

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