Tetrahedron Letters No.40, pp. 3523-3524, 1969. Pergamon Press. Printed in Great Britain.

ELECTROLYTIC GENERATION OF STRONG BASES
I. WITTIG REACTION

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(Received in UK 13 July 1969; accepted for publication 4 August 1969)

Recently the formation of ylides during the electrolysis of solutions containing phosphonium or sulphonium salts (1,2) was demonstrated. The formation of an ylide is, however, not a redox, but an acid-base reaction. During the electrolytic formation of ylides a redox reaction must take place which requires protons delivered by the phosphonium or sulphonium salt thus forming an ylide.

In order to separate the redox reaction from the acid-base reaction, a solution of azobenzene, benzaldehyde, benzyltriphenylphosphonium bromide, and lithium chloride in dimethyl formamide (DMF) was reduced at a potential where only the easily reducible azobenzene were able to accept electrons, and under conditions where the only proton donor is the phosphonium salt.

The reactions can be formulated in the following way:

REDUCTION

$$C_6H_5N{=}NC_6H_5 \xrightarrow[\text{E } -0.90\text{ V, DMF}]{2e\ +\ 2H^+} \underset{\substack{\sim 100\% \\ \text{(not isolated)}}}{C_6H_5NHNHC_6H_5} \xrightarrow{H^+} \underset{68\%}{\text{benzidine}} + \underset{\substack{\text{(not iso-} \\ \text{lated)}}}{\text{diphenyline}}$$

PROTON ABSTRACTION

$$(C_6H_5)_3\overset{+}{P}CH_2C_6H_5 \xrightarrow[\text{DMF}]{-H^+} (C_6H_5)_3P{=}CHC_6H_5$$

WITTIG REACTION

$$(C_6H_5)_3P{=}CHC_6H_5 \xrightarrow{C_6H_5CHO} \underset{98\%}{(C_6H_5)_3PO} + \underset{59\%}{\underline{\text{cis}}\text{-stilbene}} + \underset{39\%}{\underline{\text{trans}}\text{-stilbene}}$$

Azobenzene was chosen as depolarisator as it is very easily reducible, the conjugate base of hydrazobenzene is a strong base unable to react with the ylide, and it is easily removed from the reaction mixture as benzidine and diphenyline after rearrangement. The isolated yield of benzidine (68%) after consumption of 2.1 F/mole points to a quantitative formation of hydrazobenzene (3).

The isolated yield of stilbene was 98%; however, the cis/trans ratio 3:2 might be dependent on the solvent and the cation of the supporting electrolyte (4,5); this is presently being investigated.

The electrolytic method of generating bases has several inherent advantages. The amount of base generated is easy to measure by a coulometer, and any desired concentration of base can be maintained by controlling the current; side reactions caused by the addition of a conventional, strong base as butyl lithium (6) might be avoided.

Besides the Wittig reaction, the electrolytic generation of bases may be of interest in other base-induced reactions, e.g., in the Corey olefine syntheses (6,7). These possibilities are presently being investigated.

EXPERIMENTAL. A suspension of azobenzene (0.011 mole) in 250 ml anhydrous DMF containing benzyltriphenylphosphonium bromide (0.0198 mole), benzaldehyde (0.0297 mole), and lithium chloride (0.111 mole) was reduced with ice-cooling at -0.90 V (Ag/AgCl) at a mercury cathode in a divided cell. The reduction completed (n = 2.1), de-oxygenated conc. hydrochloric acid (20 ml) was added; after standing for 16 h under nitrogen, water (300 ml) was added, and the stilbene extracted with light petrol; triphenylphosphine oxide was then extracted with benzene; after evaporating most of the aqueous DMF-layer, the residue was diluted with water, and the benzidine was precipitated with excess 4 N sulphuric acid. The identity of the products was proved by IR-spectroscopy; the cis/trans ratio of the stilbenes was found by NMR-spectroscopy and GLC on carbon tetrachloride solutions.

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