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ELECTROCHEMICAL MERCURATION OF ORGANIC COMPOUNDS[1]

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The electrochemical procedure outlined in this communication offers an alternative method for preparation of organomercurials and their reduction products from olefins. The overall process, with further development, could complement the "solvomercuration-demercuration" method of H. C. Brown and coworkers.[2]

Organomercurials have been prepared previously using electrochemical methods by reaction of radicals (derived from aldehydes, ketones, halides, etc.) with a mercury pool cathode.[3] Several anodic polarographic studies on ketones and mercaptans have provided evidence for organomercurial formation.[4]

It is well known that if a sufficiently positive potential is applied to a dropping mercury electrode, the mercury anode is oxidized to mercurous and mercuric ions which exist in equilibrium (eq. 1a,b). Under suitable conditions, in which an acidic medium is employed to prevent precipitation of mercurous ion, cyclohexene has now been readily converted to the chloromercurial I (current efficiency: I(a), 65%; I(b), 8%; I(c), 60%). No attempt was made to maximize yields.[5]

The preparation [6] of I(a) is representative. A solution of 4.1 g (0.050 mole) of cyclohexene in 100 ml of 0.5 M $LiClO_4$ in acetonitrile containing 1 ml of concentrated HNO_3 was electrolyzed at a controlled potential of +1.20V vs. Ag, $AgClO_4$ (0.01M) at a stirred mercury pool anode. Additional HNO_3 (total 5 ml) was added periodically to keep the mercury pool free of grey-black mercurous salt deposit. After 3,350 coulombs had been passed, the anolyte was filtered through celite into 500 ml of 2% aqueous NaCl solution. This was extracted with $HCCl_3$, the organic extract dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*, leaving 3.5 g, m.p. 193-200°, of crude *trans*-2-chloromercuri-1-acetamido-cyclohexane I(a). Crystallization from $HCCl_3$-petroleum ether gave m.p. 198-200° (Lit[7] 200-201°).

Depending on reaction conditions, organomercurials can be electrochemically reduced to the corresponding bismercurial or hydrogen substituted demercuration product. Thus, electro-reduction of I(a) in anhydrous acetone solution containing $(nBu)_4NClO_4$ as supporting electrolyte at a mercury pool cathode with a controlled potential of -1.80V vs. sce gave the *bis*-mercurial[7] II in 42% current yield. In contrast, N-acetylcyclohexylamine[6] (III) was isolated in 71% yield on electrolysis of I(a) in aqueous KOH solution at a constant current of 0.20 amp (cathode potential -2.8 to -3.0V vs. sce).

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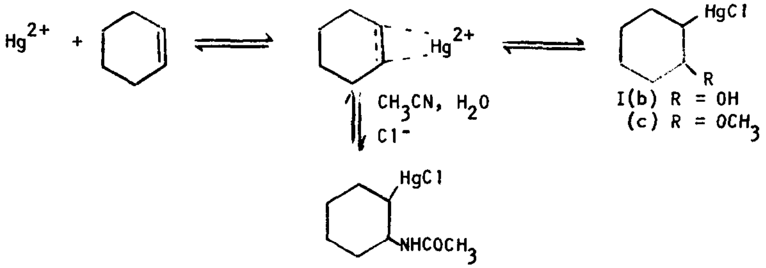
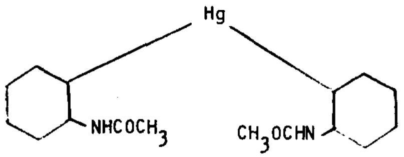
A Tafel plot for 0.5M NH_4NO_3 in methanol at a mercury pool anode exhibited a linear region with a slope of 115 mV/decade, indicating a one electron transfer in the rate-determining step. It is likely that the rate controlling process is the oxidation of the anode to Hg_2^{2+} followed by disproportionation to Hg^{2+} (eq. 1a-c). No effect was observed on the Tafel plot with addition of cyclohexene to the system.

Preliminary work suggests that anodically generated mercurials can be reduced directly without isolation, on reversal of the current flow.

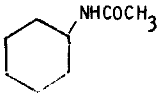
$$\left.\begin{array}{llll} Hg & \rightleftharpoons Hg^{+} & + \ e & (a) \\ 2Hg^{+} & \rightleftharpoons Hg_2^{2+} & & (b) \\ Hg_2^{2+} & \rightleftharpoons Hg & + \ Hg^{2+} & (c) \\ Hg_2^{2+} & \rightleftharpoons 2Hg^{2+} & + \ 2e & (d) \end{array}\right. \qquad (1)$$



I(a)



II



III

1: Anodic Oxidation of Organic Compounds. VII

2: H. C. Brown and P. J. Georghegan, J. Am. Chem. Soc. 89, 1522 (1967); H. C. Brown and M. Rei, ibid, 91, 5646 (1969); H. C. Brown and J. T. Kurek, ibid, 91, 5647 (1969).

3: For example see S. Wawzonek, R. C. Duty, and J. H. Wagenknecht, J. Electrochem. Soc. 111, 74 (1964); N. Hush and K. B. Oldham, J. Electroanal. Chem. 6, 34 (1963).

4: M. Heyrovsky and J. Kuta, Principles of Polarography, Academic Press, New York, N.Y., 1966, p. 171.

5: The low yield of I(b) may be the result of anodic oxidation of the mercurial. See M. Fleischmann, D. Pletcher, and G. M. Race, J. Electroanal. Chem., 23, 369 (1969).

6: The reaction should be carried out in an electrolysis cell with anode and cathode compartments separated. The electrochemical equipment has been described (N. L. Weinberg and T. B. Reddy, J. Am. Chem. Soc. 90, 91 (1968).

7: D. Chow, J. H. Robson, and G. F Wright, Can. J. Chem. 43, 312 (1965).