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NOTE

THE ELECTROLYTIC FORMATION OF ORGANOMETALLIC COMPOUNDS

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We wish to report a novel synthetic method for the preparation of organo-alkali metal and organo-alkaline earth reagents. Active "carbanion" species may be formed in high yield by electrochemical reduction in hexamethylphosphoramide (HMPA) solution containing alkali metal or alkaline earth halides as supporting electrolytes. Owing to its polar aprotic nature, HMPA is a particularly suitable solvent for examining the electrochemical reactions of carbanionic species[1].

The electrolytic reduction of 1,1-diphenylethylene in HMPA containing lithium bromide or sodium iodide electrolyte proceeds to give essentially quantitative yields of the 1,1,4,4-tetraphenylbutane dilithium or disodium salt (λ_{max} 489 mμ).

$$2\,(C_6H_5)_2C{=}CH_2+2\,M^+ +2\,e^- \rightarrow [(C_6H_5)_2\bar{C}CH_2CH_2\bar{C}(C_6H_5)_2]M_2^+ \qquad (1)$$

The resulting deep magenta solutions are stable for long periods when not exposed to adventitious impurities (*i.e.* water or oxygen). Hydrolysis of the carbanion solution gives a high yield of 1,1,4,4-tetraphenylbutane as the exclusive product. Direct alkali metal reduction in THF[2] (for the solvent separated ion-pair, λ_{max}500 mμ[3]) and HMPA solution yields an identical product.

At the anode, halide is oxidized to the free halogen.

$$2\,X^- \rightarrow X_2+2\,e^- \qquad (2)$$

In accord with equation (1), comparison of the quantity of current passed with the moles of active organometallic species formed indicates that one mole of base is formed for every equivalent of electricity passed. In previous studies by Wawzonek and co-workers[4], electrolytic reduction in other polar solvents (*e.g.* acetonitrile) resulted in the formation of several products owing to reaction of the active anion with solvent. Corresponding organo-calcium reagents [eqn. (1)] are also readily formed by using calcium iodide as a supporting electrolyte.

Electrolytic reduction of tetraphenylethylene similarly proceeds to yield a dianionic organometallic species.

$$(C_6H_5)_2C{=}C(C_6H_5)_2+2\,M^+ +2\,e^- \rightarrow [(C_6H_5)_2\bar{C}{-}\bar{C}(C_6H_5)_2]M_2^+ \qquad (3)$$

Upon electrolysis, an intermediate deep blue species is formed[5] which was shown by comparison of its electronic spectrum in HMPA with that in THF to be the tetraphenylethylene radical anion (λ_{max}665 mμ in HMPA, 660 mμ in THF[5c]). On further electrolysis, the solution becomes intense brown. Di-anion formation is established by comparison of electronic spectra (λ_{max} 455 mμ in HMPA, 490 mμ in THF[5c]).

The electrolytic reduction of triphenylmethyl chloride results in the formation of the triphenylmethyl anion (λ_{max} 504 mμ; lit.[6], 505 mμ in HMPA).

$$(C_6H_5)_3CCl+2\ M^+ +2\ e^- \rightarrow (C_6H_5)_3C^-M^+ +M^+Cl^- \tag{4}$$

The mechanism of these electrolytic reductions has not been established. Direct reduction of the olefin at the electrode surface is inferred rather than indirect reduction via alkali metal formation. Reduction of alkali metal halides in HMPA solution results in the immediate appearance of a blue color ($\lambda_{max}\approx$ 770 mμ[1a]) at the cathode. In the presence of olefins and the supporting electrolyte, only a red colored species appears at the cathode surface. Although elucidation of the mechanism of reduction would require comparison of current voltage curves of HMPA solutions containing alkali metal ions in the presence and absence of the organic moiety, recently reported reduction potentials of alkali metal ions and olefins (*e.g.* styrene[7] and α-methylstyrene[8]) in polar solvents are shown to be extremely close in magnitude. Yamazaki, Nakahama and Kambara[8] report that the reduction potential of α-methylstyrene is more positive than $NaAl(C_2H_5)_4$ in tetrahydrofuran, inferring electrolytic reduction proceeds by direct electron addition to the olefin.

These electrolytic reductions in HMPA solution proceed to the organometallic species in high yield with high current efficiency. Handling of the active metal (as in a conventional synthesis) is avoided and the extent of reaction is conveniently determined by measuring the quantity of current passed. The chemical reactivity of these electrolytically formed reagents is equivalent to those prepared by metal reduction.

EXPERIMENTAL

Procedures

A two-compartment electrolysis cell (Fig. 1) having a medium porosity glass frit partition and two 30 mm diameter platinum disc electrodes was used for bulk electrolyses. The electrodes were positioned as close to the glass frit as possible (*ca.* 3 mm) to minimize cell voltage drop. The cell was evacuated before an experiment and charged with an atmosphere of argon or nitrogen. A second cell, appended with a 0.2 cm quartz spectroscopic cell (cathode chamber), was used for visible spectral measurements on the electrolytically formed species.

A Heathkit Model PS-4 Regulated Power Supply was used for a source of d.c. A current integrator was constructed by using an Acromag Model 1201–200 Digital Type Integrator and five precision resistors as attenuators.

Spectral data were obtained using a Cary Model 14 Spectrophotometer. Extinction coefficients were not measured accurately, but were on the order of 10^4.

Electrolysis of 1,1-*diphenylethylene*

The electrolysis cell was charged with 150 ml (110 ml in cathode chamber, I) of HMPA solution, 0.2 *M* in LiBr and 0.1 *M* in 1,1-diphenylethylene. Upon passage of current (initially 100 mA at 26 V), a magenta color developed at the cathode surface. One ml aliquots of the catholyte were withdrawn at intervals with a gas tight syringe,

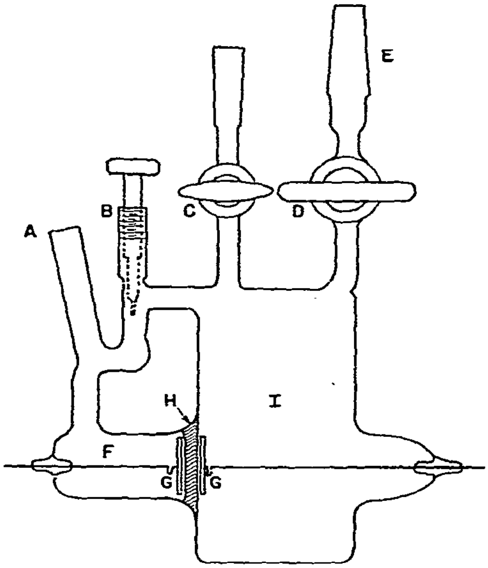

Fig. 1. Bulk Electrolysis Cell. A, entrance port (fitted with rubber septum) to F, anode chamber; B, Fisher–Porter valve separating F and I, cathode chamber; C, port (with straight-bore stopcock) for removing aliquots of catholyte; D, vacuum stopcock; E, 14/35 inner ground glass joint; G, 30 mm platinum disc electrodes; H, medium porosity glass frit.

quenched in water, and titrated with standard acid. The total number of moles of base was calculated and compared with the quantity of current passed. Upon termination of the electrolysis (after passage of 1300 coulombs), the catholyte was quenched by pouring into distilled water (under an inert gas atmosphere). The red carbanion color immediately discharged and crystals precipitated from the solution. After filtration and recrystallization from methanol, the resulting colorless plates were identified as 1,1,4,4-tetraphenylbutane, m.p. 121–122° (lit.[9], m.p. 120–121°); NMR (CCl_4): δ 7.10 (m, 20, aromatic), 3.82 [s, 2, $CH(C_6H_5)_2$], 1.97 (m, 4, CH_2) [lit.[10], NMR (CCl_4): δ 7.14, 3.88, 2.00].

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