New Cathodic Reaction of Phenylacetylene with Alkyl Halides

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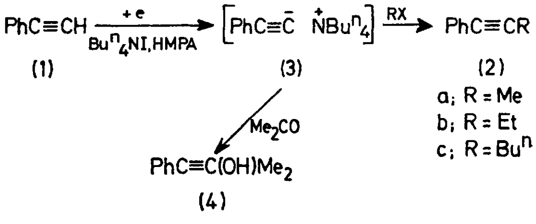
Summary Electrolysis of a mixture of phenylacetylene (**1**) and alkyl halides in hexamethylphosphoramide containing tetra-n-butylammonium iodide as supporting electrolyte produces the corresponding alkylphenylacetylenes in good yields.

ELECTROCHEMICAL reductions of acetylenic compounds under various conditions produce *cis*-[1] or *trans*-olefins[2] or saturated hydrocarbons.[1–3] It has been shown that conjugated aromatic acetylenes were readily reduced to the corresponding alkyl-benzenes.[2,3] We now report a new cathodic reaction of (**1**) without reduction of the carbon–carbon triple bond.

Constant-current electrolysis of a mixture of (**1**) and alkyl halides in hexamethylphosphoramide (HMPA) containing Bu^n_4NI as supporting electrolyte produced the corresponding alkylphenylacetylenes in high yields. These electrochemical reactions were carried out in an undivided cell or in a divided cell using two platinum plates as electrodes. Representative results are summarized in the Table. The yield of (**2**) was decreased considerably owing to side reactions when electrolysis was carried out in the absence of a supporting electrolyte. Electrolysis of a mixture of (**1**) and methyl iodide in HMPA without a supporting elec-



trolyte produced (**2**) and 1-iodo-2-phenylacetylene in 14 and 76% yields,† respectively. The latter iodoacetylene was exclusively produced in 68% yield when iodine was added to the electrolyte instead of methyl iodide. A lower yield of (**2**) resulting from prolonged electrolysis was prevented by employing a divided cell.

TABLE. Electrochemical reaction of phenylacetylene with alkyl halides[a]

RX	Current density/ A $\mathrm{cm^{-2}}$	Electrolysis time/h	Conversion of (**1**)/%	Yield of (**2**)/%[b]
MeI	0·2	1·0	46	91
	0·04—0·06[c]	6·0	81	100
EtI	0·2	1·0	39	100
	0·2	1·5	57	79[d]
	0·04—0·07[c]	6·0	71	99
EtBr	0·2	1·0	39	97
$\mathrm{Bu^nI}$	0·2	1·0	42	93

[a] Electrolysed in HMPA containing $\mathrm{Bu^n{}_4NI}$, with an undivided cell: (**1**), 1·5 mmol; $\mathrm{Bu^n{}_4NI}$, 1·0 g; RX 1·0—2·0 ml; HMPA, 8·0—10·0 ml. [b] Based on (**1**) consumed. Compounds (**2**) gave satisfactory analytical results and had the expected spectral data. [c] Electrolysed at the cathode using a divided cell. [d] Phenyliodoacetylene was produced in 21% yield.

Alkyl halides such as isopropyl iodide, s-butyl bromide, benzyl bromide, and allyl bromide did not give the corresponding products (**2**) under these electrolytic conditions; the latter two halides were probably reduced preferentially rather than (**1**). The reduction potentials of benzyl bromide and allyl bromide in tetrahydrofuran (THF) were at more positive potentials than those for (**1**) and reduction products such as bibenzyl were detected by g.l.c. analyses.

These cathodic reactions probably proceed *via* the acetylide anion (**3**), which may be formed by one-electron reduction of (**1**) in the presence of tetra-alkylammonium halide. The formation of (**3**) at the cathode is supported by the following evidences. (a) When a mixture of (**1**) and acetone in HMPA containing $\mathrm{Bu^n{}_4NI}$ was electrolysed under the same conditions as described above, the butyne (**4**) was obtained. (b) After a solution in HMPA containing (**1**) and the supporting electrolyte had been electrolysed at 0 °C, addition of methyl iodide in HMPA to the catholyte produced (**2a**) in low yield. (c) During the electrolysis, generation of hydrogen gas was observed. (d) Controlled-potential electrolysis of a solution‡ in THF containing (**1**; 1·7 mmol), methyl iodide (15 mmol), and the supporting electrolyte (0·18 M) at −1·5 V *vs.* S.C.E. produced (**2a**) alone, quantitatively. The background current with this system was 0·4 mA $\mathrm{cm^{-2}}$ at −1·5 V and the initial current with added phenylacetylene was 20 mA. These results indicate that (**1**) was reduced more preferentially in these reactions than methyl iodide, since the reduction potentials of (**1**) and methyl iodide under these electrolytic conditions were −0·95 and −1·8 V *vs.* S.C.E., respectively.

Cathodic reaction of compounds containing acidic hydrogen in the presence of tetra-alkylammonium or metal halides to form an intermediate carbanion has been reported recently.[4]

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† Yields are based on (**1**) consumed.

‡ Controlled potential electrolysis in HMPA solvent could not be carried out, probably because HMPA adsorption at the electrode surface prevented a direct electron transfer to (**1**) or alkyl halide (H. W. Sternberg, R. E. Markby, I. Wender, and D. M. Mohilner, *J. Amer. Chem. Soc.*, 1969, **91**, 4191).

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