J.C.S. Снем. Сомм., 1976

## 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<sup>2</sup> or saturated hydrocarbons.<sup>1-3</sup> It has been shown that conjugated aromatic acetylenes were readily reduced to the corresponding alkyl-benzenes.<sup>2,3</sup> We now report a new cathodic reaction of (1) without reduction of the carboncarbon triple bond.

Constant-current electrolysis of a mixture of (1) and alkyl halides in hexamethylphosphoramide (HMPA) containing Bu<sup>n</sup><sub>4</sub>NI 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<sup>a</sup>

RX	Current density/ A cm <sup>-2</sup>	Elec- trolysis time/h	Con- version of $(1)/\%$	Yield of (2)/% <sup>b</sup>
MeI	0.2	1.0	<b>46</b>	91
	$0.04 - 0.06^{\circ}$	6.0	81	100
EtI	0.2	1.0	39	100
	0.2	1.5	57	79d
	0.04-0.07°	6.0	71	99
EtBr	0.2	1.0	39	97
BunI	0.2	1.0	42	93

<sup>a</sup> Electrolysed in HMPA containing  $Bu_{4}^{n}NI$ , with an undivided cell: (1), 1.5 mmol;  $Bu_{4}^{n}NI$ , 1.0 g; RX 1.0—2.0 ml; HMPA, 8.0—10.0 ml. <sup>b</sup> Based on (1) consumed. Compounds (2) gave satisfactory analytical results and had the expected spectral data. <sup>c</sup> Electrolysed at the cathode using a divided cell. <sup>d</sup> 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

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 Bun<sub>4</sub>NI 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  $^{\circ}\mathrm{C},$ 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<sup>‡</sup> in THF containing (1; 1.7 mmol), methyl iodide (15 mmol), and the supporting electrolyte (0.18 м) at -1.5 V vs. S.C.E. produced (2a) alone, quantitatively. The background current with this system was  $0.4 \text{ mA cm}^{-2}$  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

(Received, 29th March 1976; Com. 324.)

## + 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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