BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (3), 951—952 (1979)

Electrochemical Vicinal Addition of Two Alkyl Groups to Phenyl Substituted Olefins and Diethyl Fumarate

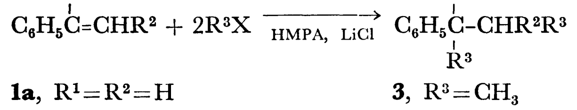
Shōhei Satoh, Tōru Taguchi, the late Mitsuomi Itoh, and Masao Tokuda*
Department of Chemical Process Engineering, Hokkaido University, Sapporo 060

(Received June 26, 1978)

Synopsis. Electrochemical reactions of styrene, 1-phenyl-1-propene, 2-phenyl-1-propene, stilbene, and diethyl fumarate with alkyl halides in hexamethylphosphoric triamide containing lithium chloride produce the corresponding vicinal adducts of two alkyl groups of alkyl halides.

Electrochemical reduction of an alkyl halide produces a radical or a carbanion intermediate, these have been employed as an useful species for a carbon-carbon bond formation. Alkyl halides also work as efficient trapping agents for the anionic intermediate generated by the electrochemical reduction of neutral organic compounds, although relatively few reports on such trapping reactions are available.[1] The work reported here was carried out to explore a carbon-carbon bond formation reaction using alkyl halide or trialkylborane by an electrochemical method.[2] In the present paper we wish to report that the electrolysis of alkyl halides with phenyl substituted olefins or diethyl fumarate produces the corresponding vicinal addition products in which two alkyl groups from alkyl halides were introduced to the double bond carbons. This reaction is of synthetic interest because an introduction of two identical alkyl groups to a carbon-carbon double bond in one step is very difficult.

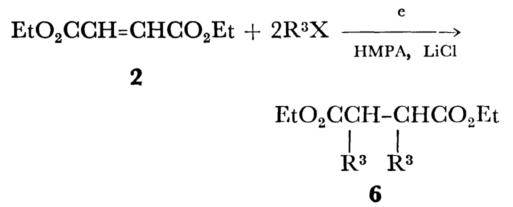
Electrolysis of a mixture of styrene (**1a**) and excess methyl iodide in hexamethylphosphoric triamide (HMPA) containing lithium chloride as a supporting electrolyte produced 2-phenylbutane (**3a**) in a good yield. Phenylpropenes **1b** and **1c**, *trans*-stilbene (**1d**), and diethyl fumarate (**2**) were found to undergo similar dialkylation reactions. These representative results are summarized in Table 1. In the electrochemical reaction of **1b** with methyl iodide, 3-methyl-3-phenylpentane (**7**) was also produced in a 11% yield along with 2-methyl-2-phenylbutane (**3b**). Alkyl benzene with a chain length of C_7 was also detected by GC-mass spectroscopy. The reactions of **1a** and **1b** using a nickel cathode produced almost the same yields of **3a**, **4a**, **5a**, and **3b** as those using a platinum cathode, while diethyl fumarate (**2**) did not produce **6**. The reaction of **2** was successfully carried out by using a mercury pool as a cathode.



$$\mathrm{C_6H_5\overset{R^1}{C}{=}CHR^2} + 2\mathrm{R^3X} \xrightarrow[\text{HMPA, LiCl}]{e} \mathrm{C_6H_5\underset{R^3}{\overset{R^1}{C}}{-}CHR^2R^3}$$

1a, $R^1=R^2=H$
1b, $R^1=CH_3$, $R^2=H$
1c, $R^1=H$, $R^2=CH_3$
1d, $R^1=H$, $R^2=C_6H_5$

3, $R^3=CH_3$
4, $R^3=C_2H_5$
5, $R^3=n\text{-}C_4H_9$



$$\mathrm{EtO_2CCH{=}CHCO_2Et} + 2\mathrm{R^3X} \xrightarrow[\text{HMPA, LiCl}]{e} \mathrm{EtO_2C\underset{R^3}{CH}{-}\underset{R^3}{CH}CO_2Et}$$

2

6

A detailed understanding of the electrode processes seems very difficult, since HMPA adsorption at the electrode surface sometimes prevented a direct electron transfer to substrates.[3] Hence, a voltammetric study or a controlled potential electrolysis in HMPA solution could not be carried out successfully. However, several points must be noted. First, the electrolysis using a divided cell showed that all products obtained were formed at a cathode. Second, from the fact that the reduction potential of **1** is more negative than those of alkyl halides while that of **2** is slightly more positive,[4,5] it may be said that the reaction mechanism of phenyl substituted olefins **1** is different from that of diethyl fumarate (**2**). At the same time, the difference of the reaction mechanisms between **1** and **2** may be also substantiated from the results in Table 1 in which nickel and mercury cathodes are used. Third, formation of **7** from **1b** may be elucidated by further electrochemical dialkylation of 2-phenyl-1-butene (**8**) which may be produced as the intermediate, since the electrochemical reaction of **8** with methyl iodide was found to produce **7** as a main product. Consequently, two pathways may be involved in these reactions. (a) Electron transfer to alkyl halide directly from a cathode, from a solvated electron,[3,6] or from lithium metal formed by reduction of lithium chloride[3,6b,7] produced an alkyl radical or a carbanion. Addition of these species to the olefin provided the intermediate radical or carbanion, the former of which may be further reduced to the latter. These carbanions are trapped by an excess of alkyl halide to produce the dialkylation product. (b) Electron transfer to olefin produced an anion radical,[8] which was trapped by alkyl halide to produce the intermediate radical. The resulting radical is reduced to the corresponding carbanion, which may be trapped again by alkyl halide to produce the dialkylation product. The former pathway (a) may be predominant in phenyl-substituted olefins and the latter (b) in diethyl fumarate.

A similar dialkylation reaction using an alkali metal was reported by Scilly *et al.*[9]

Experimental

All materials were distilled before use. HMPA was dried over calcium hydride and distilled before use. Quantitative GLPC analyses (SE-30, 15% on Uniport B) were carried out by an internal standard method.

General Procedure for Electrolysis. The electrolysis was carried out in the usual undivided cell equipped with two platinum plate electrodes (1×1 or 2×2 cm^2), a magnetic

Table 1. Electrochemical dialkylattons of phenyl-substituted olefins and diethyl fumarate$^{a)}$

Substrate	RX	Cathode	LiCl (M)	Product	Conversion of **1** or **2** (%)	Yield$^{b)}$ of product (%)
1a	$CH_3I^{c)}$	Pt	0	**3a**	59	33
	CH_3I	Pt	0.3	**3a**	28	96
	$CH_3I^{d)}$	Pt	0.3	**3a**	98	43
	CH_3I	Ni	1.5	**3a**	47	73
	C_2H_5I	Pt	0.3	**4a**	57	69
	C_2H_5Br	Pt	0.3	**4a**	68	35
	C_4H_9Br	Pt	1.5	**5a**	84	42
	C_4H_9Br	Ni	1.5	**5a**	83	48
1b	CH_3I	Pt	1.5	**3b**	49	23
	CH_3I	Ni	1.5	**3b**	58	33
	CH_3I	Hg	1.5	**3b**	5	0
1c	CH_3I	Pt	1.5	**3c**	42	32
	CH_3I	Pt	$0.2^{e)}$	**3c**	21	45
1d	CH_3I	Pt	1.5	**3d**	—	trace
2	CH_3I	Pt	0.3	**6**	39	51
	CH_3I	Pt	$0.1^{f)}$	**6**	66	36
	CH_3I	Ni	1.5	**6**	—	trace
	CH_3I	Hg	1.5	**6**	100	63

a) Current density: 0.5 A/cm^2; electricity passed: 20 F/mol. b) Yields are based on **1** or **2** comsumed. c) 0.1 A/cm^2; 20 F/mol. d) 100 F/mol. e) Instead of LiCl, tetrabutylammonium iodide was used. f) Instead of LiCl, $LiClO_4$ was used.

stirring bar, and a reflux condenser. A divided cell, when needed, was used. Olefin **1** or **2** (1 mmol) and excess alkyl halides (20—30 mmol) were dissolved in 8 ml of HMPA containing 0.1—0.5 g of LiCl. The solution was electrolyzed at a constant current (0.5 A/cm^2) with the passage of electricity of approximately 20 F/mol.

Electrochemical Reaction of Styrene (1a) with Alkyl Halides. Electrolysis of **1a** and excess methyl iodide produced 2-phenylbutane (**3a**) : NMR (CCl_4) δ 0.83 (t, 3H), 1.24 (d, 3H), 1.59 (qi, 2H), 2.55 (m, 1H), 7.08 ppm (m, 5H); $m/e=134$ (M^+). Spectral data of **3a** were fully identical to those of an authentic sample. A similar electrolysis of **1a** and excess ethyl iodide or ethyl bromide produced 3-phenylhexane (**4a**): NMR (CCl_4) δ 0.75 (t, 3H), 0.84 (t, 3H), 1.15 (m, 2H), 1.56 (m, 4H), 2.36 (qi, 1H), 7.06 ppm (m, 5H); $m/e=162$ (M^+). Electrolysis of **1a** and excess butyl bromide produced 5-phenyldecane (**5a**): NMR (CCl_4) δ 0.83 (t, 6H), 1.20 (m, 10H), 1.55 (m, 4H), 2.47 (m, 1H), 7.10 ppm (m, 5H); $m/e=218$ (M^+). Spectral data of **5a** were fully identical to those of an authentic sample prepared from **1a** and butyl bromide using lithium metal.[9)]

Electrochemical Reaction of 2-Phenyl-1-propene (1b) with Methyl Iodide. Electrolysis of **1b** and methyl iodide produced 2-methyl-2-phenylbutane (**3b**) [NMR (CCl_4) δ 0.67 (t, 3H), 1.27 (s, 6H), 1.64 (q, 2H), 7.16 ppm (m, 5H); $m/e=148$ (M^+)] and 3-methyl-3-phenylpentane (**7**) [NMR (CCl_4) δ 0.67 (t, 6H), 1.23 (s, 3H), 1.65 (m, 4H), 7.19 ppm (m, 5H); $m/e=162$ (M^+)]. Spectral data of the latter product **7** were identical to those of the product obtained by electrochemical reaction of 2-phenyl-1-butene (**8**) with methyl iodide.

Electrochemical Reaction of 1-Phenyl-1-propene (1c) with Methyl Iodide. Electrolysis of **1c** and methyl iodide produced 2-methyl-3-phenylbutane (**3c**): NMR (CCl_4) δ 0.75 (d, 3H), 0.94 (d, 3H), 1.23 (d, 3H), 1.79 (m, 1H), 2.38 (qi, 1H), 7.13 ppm (m, 5H); $m/e=148$ (M^+).

Electrochemical Reaction of trans-*Stilbene (1d) with Methyl Iodide.* Electrolysis of **1d** and methyl iodide produced a trace of 2,3-diphenylbutane (**3d**). The retention time and mass spectrum of **3d** were identical to those of an authentic sample prepared from **1d** and methyl iodide using lithium metal.[9)] Spectral data of **3d** are as follows: NMR (CCl_4) δ 1.02 (d, 6H, *meso*), 1.27 (d, 6H, *dl*), 2.88 (m, 2H), 6.9—7.2 ppm (m, 10H); $m/e=210$ (M^+).

Electrochemical Reaction of Diethyl Fumarate (2) with Methyl Iodide. Electrolysis of **2** and methyl iodide produced diethyl 2,3-dimethylbutanedioate (**6**): NMR (CCl_4) δ 1.11 (d, 6H), 1.25 (t, 6H), 2.59 (m, 2H), 4.08 ppm (q, 4H); IR (CCl_4) 1735, 1160 cm^{-1}; $m/e=157$ (M^+-45).

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