

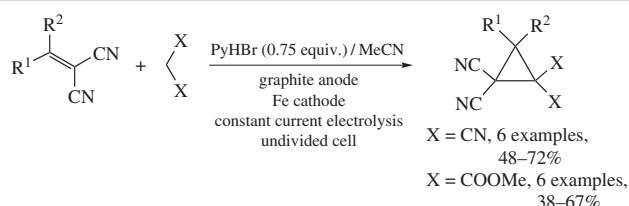
Pyridinium bromide as a new mediator for electrochemical transformations involving CH-acids

Anatoly N. Vereshchagin,* Evgeniya O. Dorofeeva,
Michail N. Elinson, Victor A. Korolev and Mikhail P. Egorov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: vereshchagin@ioc.ac.ru

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Pyridinium bromide has been tested as a new mediator for electrochemical synthesis of functionalized cyclopropane from alkylidenemalononitriles and CH-acids. The process was performed in an undivided cell with the use of substoichiometric amount of PyHBr that serves both as a mediator and a supporting electrolyte, and MeOH or MeCN as the solvents.



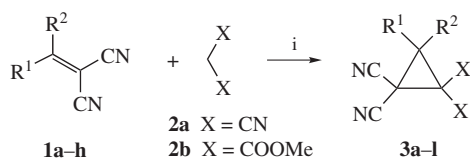
Electrosynthesis is a competitive method of modern organic chemistry.^{1–3} The importance of electrochemical synthesis can hardly be overestimated because of its great and, in some cases, unique possibilities for performing various transformations of organic compounds.^{4,5} In recent decades, indirect electrooxidation of organic compounds involving mediators has been the subject of intensive studies.⁶

Cheap and available halides are well-known and popular inorganic mediators⁷ that provide processing in an undivided cell. On the other hand, CH-acids are convenient objects for the preparation of various compounds by indirect electrooxidation in alcohols in the presence of sodium halides as mediators.^{8,9}

Despite the advantages and significant achievements described, the use of alkali metal halides as mediators in alcohol solutions for carrying out organic electrosyntheses has several disadvantages. The use of methanol or ethanol as solvents is not good for poorly soluble substrates. Significant limitations can be caused by certain side processes.¹⁰ Quaternary ammonium salts are widely used in

electrochemistry as supporting electrolytes. Recently, the electro-initiated oxidative amination of benzoxazoles¹¹ and sulfonamides¹² using tetraalkylammonium halides and ammonium iodide as redox catalysts, respectively, was reported.

Here, we present pyridinium bromide as a new mediator for electrochemical transformations. We started our studies employing benzylidenemalononitrile **1a** and malononitrile **2a** as the model reactants for constant current electrolysis (100 mA cm^{−2}) in an undivided cell equipped with graphite rod as the anode and iron plate as the cathode (Scheme 1, Table 1). Initially, we optimized the catalytic efficacy of PyHBr in methanol (entries 1–10). The current density of 50 mA cm^{−2}, 0.75 equiv. of PyHBr, 20 °C, 2.2 F mol^{−1} were found to be the optimum conditions for obtaining product **3a** (entry 5). The use of smaller amount of PyHBr leads to drop in the yields (entries 1, 2), apparently, due to incomplete regeneration of the mediator. Raising the current density up to 100 mA cm^{−2} (entry 4) or temperature up to 30 °C (entry 8) also results in decrease in the yield, which may be caused



1	R ¹	R ²	3	R ¹	R ²	X	Yield (%)
a	Ph	H	a	Ph	H	CN	72
b	4-MeC ₆ H ₄	H	b	4-MeC ₆ H ₄	H	CN	66
c	4-ClC ₆ H ₄	H	c	4-ClC ₆ H ₄	H	CN	64
d	3-BrC ₆ H ₄	H	d	3-BrC ₆ H ₄	H	CN	58
e	4-NO ₂ C ₆ H ₄	H	e	4-NO ₂ C ₆ H ₄	H	CN	48
f	(CH ₂) ₅		f	(CH ₂) ₅		CN	60
g	3-MeOC ₆ H ₄	H	g	Ph	H	COOMe	67
h	3-NO ₂ C ₆ H ₄	H	h	4-MeC ₆ H ₄	H	COOMe	63
			i	3-MeOC ₆ H ₄	H	COOMe	67
			j	3-BrC ₆ H ₄	H	COOMe	64
			k	3-NO ₂ C ₆ H ₄	H	COOMe	44
			l	4-NO ₂ C ₆ H ₄	H	COOMe	38

Scheme 1 Reagents and conditions: i, **1** (10 mmol), **2** (10 mmol), PyHBr (7.5 mmol), MeCN (20 ml), undivided cell, 20 °C, 2.2 F mol^{−1}, current density of 50 mA cm^{−2}.

Table 1 Electrocatalytic transformation of benzylidenemalononitrile **1a** and malononitrile **2a** into tetracyanocyclopropane **3a** with PyHBr as mediator.^a

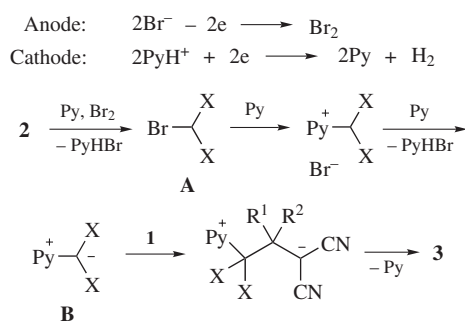
Entry	Solvent	Equiv. of PyHBr	T/°C	Current density/ mA cm ^{−2}	Electricity passed/ F mol ^{−1}	Isolated yield of 3a (%)
1	MeOH	0.30	20	100	2.0	25 ^b
2	MeOH	0.50	20	100	2.0	42
3	MeOH	0.75	20	100	2.0	60
4	MeOH	1.00	20	100	2.0	60
5	MeOH	0.75	20	100	2.2	68
6	MeOH	0.75	20	100	2.5	61
7	MeOH	0.75	10	100	2.2	44
8	MeOH	0.75	30	100	2.2	32 ^b
9	MeOH	0.75	20	50	2.2	72
10	MeOH	0.75	20	25	2.2	68
11	EtOH	0.75	20	50	2.2	62
12	MeCN	0.75	20	50	2.2	72
13	DMF	0.75	20	50	2.2	35 ^b
14	DMSO	0.75	20	50	2.2	25 ^b

^a Benzylidenemalononitrile **1a** (10 mmol), malononitrile **2a** (10 mmol), solvent (20 ml), undivided cell. ^b NMR data.

by acceleration of side electrochemical oligomerization of the reactants. The low yield and insufficient conversion of starting compounds were observed when electrolysis was carried out at 10 °C (entry 7). Ethanol is slightly less effective medium than methanol (entry 11). Since PyHBr is soluble in aprotic solvents, electrolysis was performed in MeCN leading to product **3a** in good yield (entry 12).

The reaction scope with regard to dimethyl malonate **2b** was also explored. Under the optimal conditions, tetracyanocyclopropanes **3a–f** or dimethyl 2,2-dicyano-3-arylcyclopropane-1,1-dicarboxylates **3g–i** were obtained from alkylidenemalononitriles **1a–h** (both with electron-withdrawing and electron-donating substituents in aromatic ring) and CH-acids **2a,b** (see Scheme 1).[†]

Possible mechanism for the current transformation is outlined in Scheme 2. Bromine is formed at the anode, which can be observed by some colouration. The cathodic deprotonation of pyridinium cation leads to formation of free pyridine. The evolution of hydrogen at the cathode is observed, especially when electrolysis is conducted without stirring of the reaction mixture. Deprotonation of CH-acid with pyridine in solution and further bromination of CH-acid anion leads to intermediate CHBr



[†] *General procedure.* An undivided cell was equipped with a graphite anode and iron cathode (5 cm² area each) and connected to a DC regulated power supply. The cell was charged with the corresponding alkylidenemalononitrile **1** (10 mmol), CH-acid **2** (10 mmol), PyHBr (7.5 mmol), and MeCN (20 ml). The mixture was electrolyzed using constant current conditions (50 mA cm⁻²) at room temperature under magnetic stirring (TLC control, full consumption of olefin **1**). The reaction solution was then concentrated under reduced pressure, the residue was treated with water, and the product was extracted with dichloromethane (3 × 20 ml), the extract was dried over Na₂SO₄ and concentrated. The residue was purified by crystallization from methanol to afford the desired cyclopropane **3**.

For characteristics of products **3**, see Online Supplementary Materials.

acid **A**. Next, ylide **B** can be formed from intermediate **A** and pyridine. Finally, addition of ylide **B** at alkylidenemalononitrile gives rise to cyclopropane **3**. The last stage was postulated previously in the chemical synthesis of cyclopropanes from pyridinium ylides and benzylidenemalononitriles.¹³

To summarize, we have employed pyridinium bromide as a new mediator for electrosynthesis of functionalized cyclopropanes from CH-acids and benzylidenemalononitriles. The procedures for electrolysis and isolation of products are simple and can be used both under laboratory conditions and in larger reactors.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.07.010.

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