

Electrosynthesis of Stabilized Diazo Compounds from Hydrazones

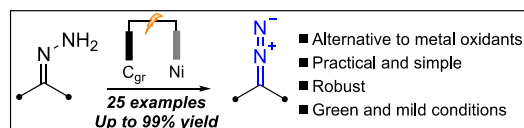
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Supporting Information Placeholder

ABSTRACT: An electrochemical synthesis of diazo compounds from hydrazones in yields as high as 99% was performed. This method was elaborated as a useful synthetic method and demonstrated on various diazo substrates (25 examples). Apart from exhibiting matched efficiency as commonly used harsh and toxic chemical oxidants, this reaction is practically simple to set up, mild in conditions, high in electron efficiency (3 F/mol).



Accessing complex and pharmaceutically relevant organic compounds relies on multistep synthetic routes that use expensive and hazardous reagents.¹ The increase in environmental awareness has led industries to search for better alternatives that reduce waste generation, reduce carbon footprint, and avoid highly toxic chemicals and metals. So, it is no surprise that synthetic organic chemistry has seen a recent revival of the use of electrochemistry.²⁻⁴ Electrochemistry is defined as applying an electric difference of potential that induces the addition or removal of electrons to or from a molecule.⁵ It can enable the replacement of expensive and toxic reducing and oxidizing reagents by the simplest form of an electron source: electricity. The inevitable shift towards sustainable energy sources to generate electricity makes research in this area all the more valuable. Hence, we are in the era of the revitalization of electrochemistry with a large availability of uncharted waters in the field.⁶⁻⁸

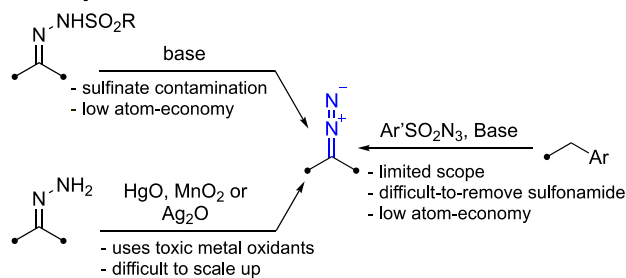
One area of research that has particularly attracted our attention is the development of synthetic strategies for the synthesis of diazo compounds. Diazo compounds are notorious for their synthetic versatility and high reactivity.⁹⁻¹¹ They are commonly used as carbene precursors to shortcut chemical syntheses by the performance of unique disconnection approaches through cyclopropanation,¹²⁻¹⁴ dipolar cycloaddition,^{15,16} and insertion reactions.^{17,18} Although reports on the use of diazo compounds are numerous, those covering their synthesis are limited and unsustainable. Until now, the most used approaches for the synthesis of diazo compounds are the Bamford-Stevens reaction of sulfonyl hydrazones,¹⁹ Regitz diazo transfer,²⁰ and oxidation of simple hydrazones (Figure 1).²¹⁻²⁵ The Bamford-Stevens reaction and Regitz diazo transfer score low on scales of atom-economy and require tedious purifications. Even the most straightforward oxidation of simple hydrazones into diazo compounds usually requires stoichiometric amounts of oxidants that are not only expensive but also toxic, i.e. Ag₂O,

MnO₂, Pb(OAc)₄, and HgO.^{23,26-28} More recently, hypervalent iodine(III) reagents, such as PhIO and PhIF₂, were reported as metal-free oxidants to access diazo compounds.^{24,29} However, these methods suffer from the formation of PhI as a by-product which needs to be removed by purification. We herein propose to employ electrochemistry as a green oxidant to achieve a clean, streamlined, atom economic, and affordable synthesis of diazo compounds from simple hydrazones.

There are very few reports on the electrochemical oxidation of simple hydrazones. In 1983, Chiba *et al.* demonstrated that the anodic oxidation of benzophenone hydrazones on a platinum anode leads to the corresponding azine in high yields.³⁰ Interestingly, they observed that when using an undivided cell containing NaOMe-MeOH at 70 °C, diphenyl diazomethane could be made in situ by the formation of diphenylmethyl methyl ethers upon reaction with MeOH, in addition to cyclopropanes in the presence of alkenes.

Later, Okimoto and Takahashi successfully isolated benzoylphenyl diazomethanes during the anodic oxidation of benzil hydrazones in the presence of KI as a halide ion source.³¹ Although the respective dimethyl acetals were obtained when KBr was used, it was assumed that the reaction proceeds via the formation of a diazo

Commonly used methods:



This work: Anodic oxidation of hydrazones into diazo compounds

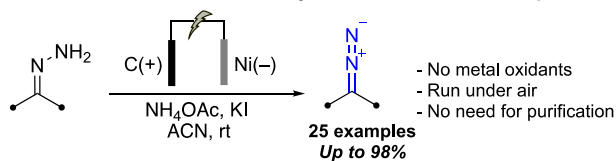


Figure 1. Overview of methods for synthesizing diazo compounds

intermediate. They successfully obtained high yields of the diazo compound, but their study was restricted to two examples. The same group then reported the anodic oxidation of dihydrazones into bis-diazo compounds, but again, only for two examples.³²

The main reasons why these electrochemical methods have not gained popularity and been incorporated as synthetic methods is because they lack generality and scope, are difficult to reproduce, use expensive electrode material, and require divided cells which are not regularly found in synthetic laboratories. To address this, we have developed, as an unprecedented synthetic method, the organic electro-synthesis of diazo compounds through anodic oxidation of simple hydrazones which is practical to set up (no need for moisture exclusion or inert atmosphere), has high electron efficiency, is performed with a standardized electrochemical setup, uses readily available and cheap electrode material, and produces high yields of the desired diazo compound (Figure 1).

The anodic oxidation of methyl hydrazoneylidene-2-phenylacetate **1a** was initially studied using a graphite anode, which would be more appealing than using expensive electrode material such as Pt, while examining different solvent-electrolyte combinations (Table 1). Using solvents such as dimethyl carbonate (DMC), diethyl carbonate (DEC), propylene carbonate (PC), and DMSO, the reaction could not reach the level of conductivity needed to achieve the selected current (25 mA, 10.4 mA/cm²). MeOH promoted better conductivities than other solvents, and the diazo **2a** was obtained in modest yields. Even though MeOH tends to promote better conductivities for electro-organic reactions, we wanted to move away from choosing a protic solvent for this reaction because the objective is to develop a methodology for the synthesis of diazo compounds which can be used as is for subsequent reactions in carbene chemistry.

The presence of a protic solvent would limit this method because it would react with the carbene by polar X-H insertions and necessitate the diazo compound's isolation. An acetonitrile/water mixture appeared promising as a solvent choice for further optimization. However, reactions with graphite as the cathode led to poor yields.

Table 1. Optimization of electrolysis conditions for the electro-synthesis of diazo compound **2a.**

	0%			89%	
Cathode material	C _{gr}		Pt	Ni	
Solvent	DEC DMC PC	DMSO	MeOH MeOH/HFIP	CH ₃ CN/H ₂ O	CH ₃ CN
Electrolyte	KI NaOMe LiClO ₄ NEt ₃ collidine NH ₄ Cl	KBr LiCl	(NH ₄) ₂ CO ₃ NH ₄ I	NH ₄ OAc	NH ₄ OAc/KI
Current	25 mA		100 mA	50 mA	
Concentration	0.16 M		0.04 M	0.08 M	

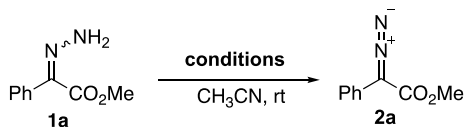
^aReactions are carried out on a 0.4 mmol scale of **1a** (3 F/mol) at rt in a 5 mL ElectraSyn cell equipped with C and Ni electrodes, and yields were determined by ¹H NMR with CH₂Br₂ as an internal standard.

This was due to the reduction of the formed diazo compound **2a** into the simple ester. Using a material with a low hydrogen overvoltage, such as Pt or Ni, as the cathode enhanced the yield of the diazo compound and decreased the yield of the reduction product. This reaction showed to proceed better in the presence of NH₄OAc and this is explained by two reasons: the first is that acetate behaves as a base to help mediate the oxidation of the hydrazone; the second is that the ammonium cation acts a proton source which is more easily reduced at the cathode compared to the diazo compound. An excess of NH₄OAc was required to get better yields of diazo **2a** (5 equiv). In the absence of water, the reaction still displayed high resistance, but with the addition of KI, this was resolved and the diazo compound **2a** was obtained in 89% yield and in high purity (no need for purification). To move away from using expensive and precious metal electrode material, the Pt cathode was replaced by a cheaper Ni electrode, resulting in unchanged yields of the desired diazoester **2a**. So, as optimal reaction conditions, a graphite anode and Ni cathode in acetonitrile with KI (0.5 equiv) and NH₄OAc (5 equiv) at 50 mA (20.8 mA/cm²) for 3 F/mol results in high yields (89%) of the desired diazo compound **2a**. Further details on optimizing the reaction's conditions, such as changes in quantities of electrolytes and concentrations, can be found in detail in the Supporting Information.

A few control reactions were run to show that this reaction is electrochemical (Table 2). Under the optimized electrochemical conditions, using C (+) and Ni (-) electrodes with KI and NH₄OAc as electrolytes in CH₃CN, after running 3 F/mol at 50 mA (20.8 mA/cm²), the diazoester **2a** is produced in 89% yield (Table 2, entry 1). The reaction of the hydrazone in the presence of KI (0.5 equiv) and the absence of any applied current leaves the hydrazone intact after 24 h (Table 2, entry 2). The same result is observed when using both KI (0.5 equiv) and NH₄OAc (5 equiv) (Table 2, entry 3).

To investigate whether the possible formation of I₂ under the optimized electrochemical conditions would be responsible for the oxidation reaction, we introduced 1 equiv of I₂ with the hydrazone in the absence of any current. This resulted in azine formation with no trace of the diazo compound **2a** (Table 2, entry 4). However, running the same reaction in the presence of NH₄OAc resulted in the

Table 2. Control experiments for the anodic oxidation of hydrazone 1a.^a



Entry	Conditions	Yield (%)
1	C (+), Ni (-), KI (0.5 equiv), NH ₄ OAc (5 equiv), 20.8 mA/cm ² , 3 F/mol	89
2	No current, KI (0.5 equiv), 24 h	NR
3	No current, KI (0.5 equiv), NH ₄ OAc (5 equiv), 24 h	NR
4	No current, I ₂ (1 equiv), 1 h	0
5	No current, I ₂ (1 equiv), NH ₄ OAc (5 equiv), 1 h	15

^aReactions are carried out on 0.4 mmol scale of **1a** in CH₃CN (0.08 M) and yields were determined by ¹H NMR with CH₂Br₂ as an internal standard.

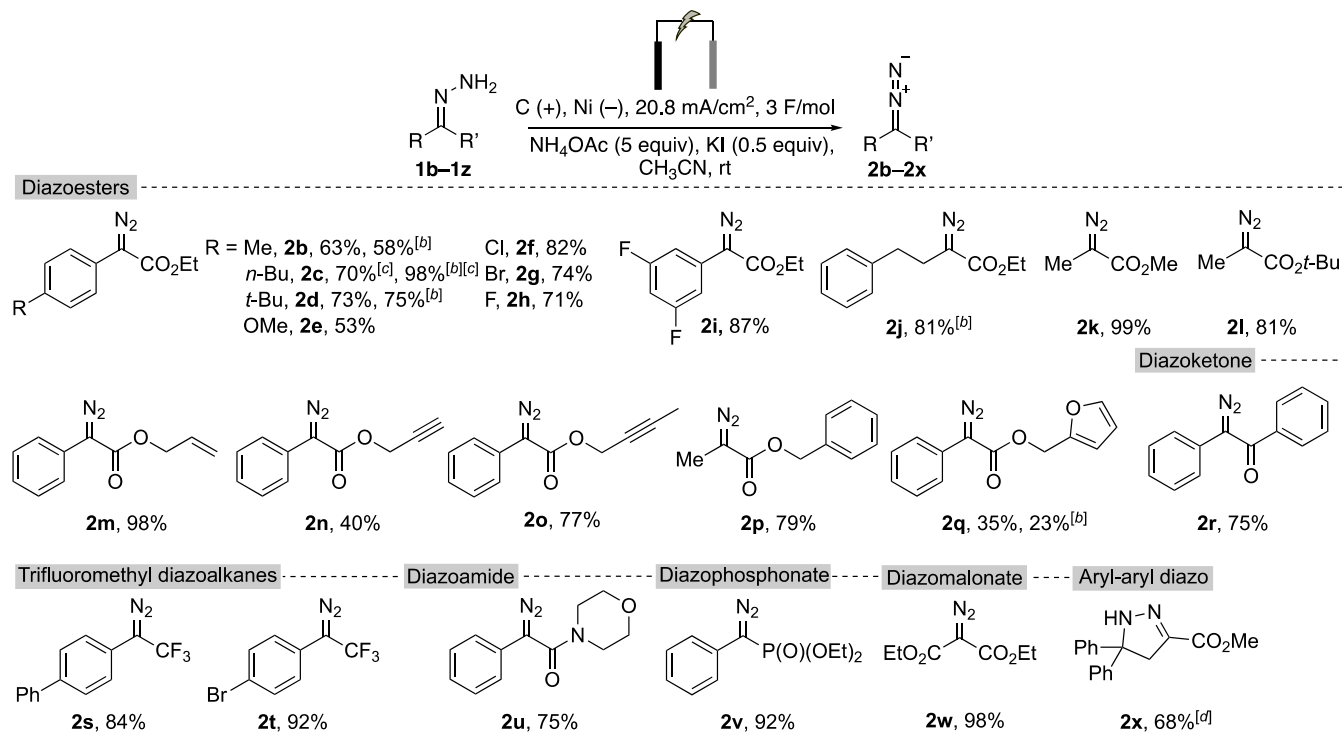
formation of the diazo compound **2a** in 15% yield (Table 2, entry 5). Although we cannot rule out the direct reaction with electrogenerated iodine, the electrochemical reaction led to a cleaner product and higher yield.

With the optimized electrochemical conditions in hand, we investigated the scope of this reaction for the synthesis of different diazo compounds (Scheme 1). In the case of aryl-ester diazo compounds, *para* substituents with electron-donating character on the aryl ring (**2a–2e**) resulted in slightly decreased yields (53–73%). In an attempt to improve these yields, the electrolysis of **1b** and **1d** was run at a lower current (25 mA, 10.4 mA/cm²); however, no significant change in yields was observed. In the case of a *p*-(*n*-Bu)phenyl ethyl diazoacetate **2c**, the reaction required 4 F/mol instead of 3 F/mol to improve conversion and obtain diazo compound **2c** in 70% yield. For the latter case, decreasing the current to 25 mA at 4 F/mol led to a significantly improved yield of **2c** (98%).

Electron-withdrawing groups in *para* position (-Br, -Cl, and -F) and *m,m'*-F substituted hydrazone **1i** resulted in good yields of their corresponding diazo compounds **2f–2i**. Homobenzylic and aliphatic diazoesters could also be easily accessed using this method in high yields with no need for purification (81–99% yield). Hydrazone **1p** with a benzylic ester group was successfully oxidized into the desired diazo compound **2p** in a moderate yield (79%). Using a furfuryl ester was also tolerated using this method, and the diazo compound **2q** was obtained in 35% yield, which slightly decreased when running the electrolysis at 25 mA (10.4 mA/cm²). Using hydrazones with unsaturated ester parts with either an alkene or an alkyne, the corresponding diazoester was obtained in 98% yield with an allyl ester (**2m**) and 40% yield with a terminal propargyl ester (**2n**); however, improved yields could be obtained with an internal alkyne as seen for **2o** with was obtained in 77% yield. This method is also useful for synthesizing benzil diazo **2r** and trifluoromethyl diazoalkanes **2s** and **2t** in high yields (75%, 84%, and 92%, respectively). Diazoamide **2u** and phosphonate **2v** could also be synthesized in high yields (75 and 92%, respectively) using this method. Diazomalonate **2w** was obtained in a quantitative yield, and the oxidation of benzophenone hydrazone to make the diazo, which was trapped with methyl acrylate, gave pyrazole **2x** in 68% yield. Hence, this shows that the electrochemical method has significant potential as a valuable way to access various diazo compounds free of any metal oxidants and organic contaminants. Compared to other synthetic methods commonly used to access these diazo compounds, anodic oxidation of hydrazones shows matched potential with the advantage of using metal-free and green conditions free of any harsh or toxic chemical reagents. In addition, this method is extremely robust and does not need dry and inert conditions. In most cases, at the end of the reaction, a simple extraction to remove the inorganic salts sufficed to obtain the diazo compound in good purity levels.

A plausible reaction mechanism for an anodic oxidation of simple hydrazones into diazo compounds is shown in Figure 2. The oxidation is possibly indirect and mediated by an iodonium. KI, in the presence of acetonitrile, is oxidized at the anode into an iodonium species ((CH₃CN)₂I⁺) and is responsible for the formation of the protonated diazo compound.³³ The latter is deprotonated by NH₄OAc which also behaves as a proton source that is reduced at the cathode (especially that a Ni electrode has a low overvoltage for

Scheme 1. Substrate scope for the electrosynthesis of diazo compounds.^a



^a Reactions are carried out on 0.4 mmol scale of **1a** (3 F/mol) at rt in a 5 mL ElectraSyn cell equipped with C and Ni electrodes and yields are isolated. ^b Reaction was run at 25 mA (10.4 mA/cm²). ^c Reaction was run to 4 F/mol due to incomplete conversion. ^d The diazo compound was trapped with 5 equiv of methyl acrylate

H₂ production). CV analyses of KI in acetonitrile showed the expected chemically irreversible oxidation waves at E_{pa} = 0.32 V and 0.49 V vs Fc^{+/0} [I⁻/I₃⁻ and I₃⁻/[(CH₃CN)₂I]₃]. The anodic oxidation of **1a** showed a chemically irreversible event at E_{pa} = 1.13 V vs Fc^{+/0}. Interestingly, when KI was added to the mixture, the oxidation potential of the hydrazone shifted to a more positive potential (E_{pa} = 1.14 V vs Fc^{+/0}), which would fit with the formation of an *N*-iodo hydrazone.

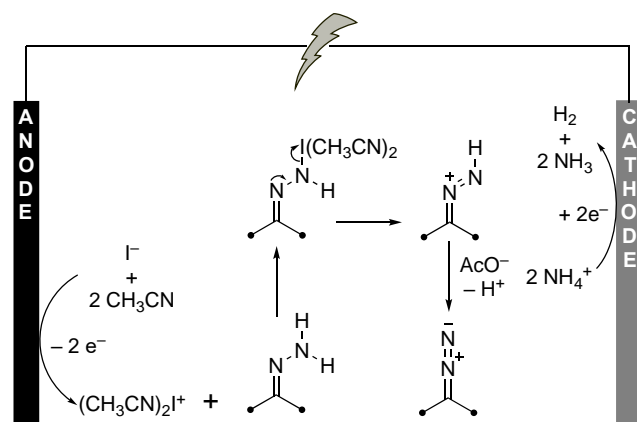


Figure 2. Proposed reaction mechanism for the anodic oxidation of hydrazones

In conclusion, we have developed a new synthetic method to access stabilized diazo compounds through the anodic oxidation of simple hydrazones. This reaction potentially replaces commonly used toxic heavy metal oxidants with electricity to synthesize highly versatile diazo compounds. Sub-equivalent amounts of KI are enough to

mediate this reaction. The electrochemical reaction conditions benefit from being mild, practical, efficient. A simple electrochemical setup and cheap electrodes are used to make this method as accessible as possible for application in any synthetic laboratory. A wide range of diazo compounds, such as diazocarbonyls and trifluoromethyl diazoalkanes, with different functional groups, could be accessed using this method. Further work covering the synthesis of semi-stabilized and non-stabilized diazo compounds is underway and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, characterization data of starting material and target compounds, and copies of ¹H, ¹³C, and ¹⁹F NMR spectra can be found in the Supporting Information. (PDF)

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All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

N.T. is grateful to the Natural Sciences and Engineering Research Council of Canada for a doctoral award (PGSD3 - 546986-2020) and the Royal Society of Chemistry for a Researcher Mobility Grant (M19- 0357) to work with K.L. We are grateful to the Engineering and Physical Sciences Research Council (Grant EP/S017097/1 to K.L. and M.C.L.), the Leverhulme Trust (Grant RPG-2021-146 to K.L., T.O., M.C.L., and J.W.) and the University of Greenwich (Vice Chancellor's Ph.D. Scholarship to A.P.) for financial support. K.L. also thanks IKA for material support. T.O. thanks the Natural Sciences and Engineering Research Council of Canada (NSERC, Discovery Grant RGPIN-2017-04272), the FRQNT Centre in Green Chemistry and Catalysis (CGCC, Strategic Cluster FRQNT-2020-RS4-265155-CCVC, and Université Laval.

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