JOC Article

Alkylation of Nitroaromatics with Tetraalkylborate Ion via Electrochemical Oxidation

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Aromatic nucleophilic substitution reaction (S_NAr) is one of the most thoroughly studied reactions. Alkylation of nitroaromatics with Grignard reagents via chemical oxidation of the σ^H-complexes is the most general method to introduce an alkyl group into a nitroaromatic compound. This approach has considerable drawbacks, especially when more than one nitro group are present in the aromatic ring. In this article, we present an electrochemical approach, which offers a new very selective methodology for obtaining alkyl polynitroaromatic compounds. Different strategies based on the use of tetralkylborate anion as nucleophiles are used so as to increase efficiency and to reduce the drawbacks associated with this reaction. A wide list of dinitro- and trinitro-aromatic compounds are studied, the range of yields obtained being from fair (40%) to excellent (85%). The key to improvement in the process is the use of electrochemical techniques for the oxidation of the mixture σ^H-complexes/tetrabutylborate ion. The electroactive character of the nucleophile, which can be oxidized to an alkyl radical, means that the S_NAr of the hydrogen polar mechanism is not the only mechanism operating during the electroxidation process, since the hydrogen radical S_NAr mechanism is running at the same time. Electrochemical mechanistic studies allow the participation of each mechanism in the global product yield obtained to be quantified.

Introduction

The main industrial process for obtaining alkyl nitroaromatic compounds is based on nitration. However, this process is poorly selective and requires very drastic conditions.[1] These serious drawbacks are the main reason new methods of alkylation of aromatic nitro compound are of remarkable interest.[2]

The traditional and widely used approach for the functionalization of aromatic compounds, which contain electron-withdrawing groups, is the nucleophilic aromatic substitution reaction (S_NAr).[3] However, lack of generality and low yields, even when chemical oxidants are used, linked with the fact that their use represents a significant environmental hazard particularly when scaling-up, make this approach difficult to apply in many cases. Furthermore, the low oxidation potential usually shown by chemicals oxidants and the high stability of the σ-complexes makes its oxidation impossible in some cases; consequently, it is also impossible to obtain the substituted product.[4]

In recent years, we have been trying to develop a general and environmentally favorable route for the nucleophlic aromatic substitution reaction, avoiding the use of chemical oxidants. It has recently been demonstrated that the use of an electrode instead of a chemical, in what we have called an electrochemical approach to nucleophic aromatic substitution, allows the oxidation of σ-complexes, leading to substitution products in good yields, when cyanide, amine, amide, or enolate anions are used as nucleophiles. Electrochemical oxidation of σ-complexes can be considered a green process, since the formation of the reduced form of the chemical oxidant is avoided. Moreover, by using electrochemical techniques, all of the potential range can be covered, thus allowing the oxidation of all kinds of σ-complexes.[5]

We have reported that two general mechanisms take place in the electrochemical S_NAr reaction, the nucleophilic aromatic substitution of hydrogen (NASH) and the nucleophilic aromatic substitution of heteroatom (NASX), Scheme 1. In a first fast equilibrium step, the σ^H-complex and/or the σ^X-complex are formed, depending on the

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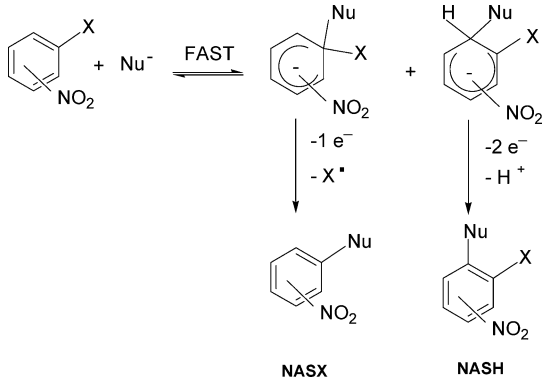
SCHEME 1



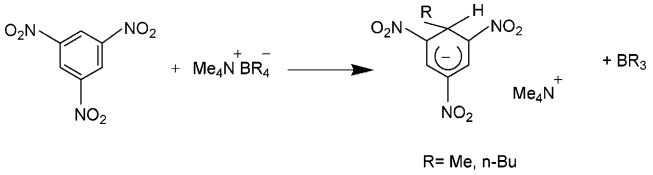
selectivity of the reaction. In the NASH process, the oxidation of the σ^H-complex then arises via a three-step mechanism. The first step is a single-electron oxidation of the σ^H-complex, followed by a H^+ elimination. The resulting radical anion could be oxidized in a second single-electron process on the electrode or, in some cases, the radical generated in the first oxidation can act as oxidizing agent, leading formally to a disproportioning process. The NASX mechanism consists of a one-electron oxidation process and the subsequent elimination of the heteroatom as a radical.[5d,e]

The reaction of organolithium or organomagnesium compounds with nitroaromatics would seem to be the first choice in order to produce alkylnitroaromatics via S_NAr. However, the first such reaction, performed by Severin, provided evidence for the difficulty of reaction control.[6] Thus, Grignard reagents (RMgX, with R = Me, Et, Bu) reacts with 1,3,5-trinitrobenzene in THF yielded the corresponding 1,3,5-trialkyl-2,4,6-trinitrocyclohexanes, after acidification of the reaction mixture. Similar reactivity was found for 1,3-dinitrobenzene and 1-chloro-2,4-dinitrobenzene. Using nitrobenzene, the reaction leads to a mixture of alkyl nitrobenzenes and alkyl nitrosobenzenes.[7]

The chemical oxidation (with Br_2 or $KMNO_4$) of σ-complexes has been reported. This leads to a mixture of reaction products, from which alkyl-substituted nitrocompounds are obtained in low yields.[8] The use of DDQ as an oxidizing agent improves the selectivity of the reaction, but the cost of DDQ and the difficulty of the separation of the reaction mixture hampers the use of this reagent in preparative experiments.[9]

Recently, a good yield synthesis of alkyl nitro benzenes, via nucleophilic aromatic substitution, has been reported, using *p*-dinitrobenzene and alkyl boranes as reagents in the presence of ^{t}BuOK in ^{t}BuOH. A mechanism based on the reaction of the alkyl radical and the radical anion of *p*-dinitrobenzene has been proposed, although no evidence was provided.[10]

SCHEME 2



We have recently reported the alkylation of nitroarenes by the electrochemical oxidation of the σ-complexes arising from the reaction of the aromatic compounds with RLi or RMgX. Both the NASH and the NASX mechanisms (Scheme 1) have been observed in these reactions. The yields obtained are comparable to or better than those previously reported by using chemical oxidants. In addition and for the first time, electrochemical oxidation allowed the NASH alkylation of dinitroderivates to be obtained in reasonable yields. Despite the use of electrochemical techniques being very attractive in S_NAr, certain problems still remain unsolved: (1) no alkyltrinitrobenzene derivatives have been obtained in any case; (2) selectivity control is difficult because of the high reactivity of the nucleophiles; and (3) RLi and RMgX require the use of high resistive solvents, which are not appropriate for performing exhaustive electrolysis (i.e., long reaction times).[11]

In 1970, Taylor reported that 1,3,5-trinitrobenzene reacts with tetraalkylborates to form the corresponding σ^H-complex (Scheme 2).[12]

The use of the tetralkylborate anion as nucleophile constitutes an interesting alternative to organolithium or organomagnesium reagents in the S_NAr reaction. However, there is no report based on this approach, probably because the chemical oxidant's power was limited to 0.6 V vs SCE [4] and all the trinitro σ-adducts have higher oxidation potentials.[5,11] This problem can be solved by using electrochemical oxidation.[5,11]

Here we report on the use of tetralkylborates in the S_NAr reaction to form alkyl dinitro and trinitro aromatic compounds. This approach increases not only the yield but also the selectivity of the reaction, when compared with RLi or RMgX alkylating agents. To establish the mechanistic details and the synthetic scope of the electrochemical method, this study was carried out for a wide series of nitrobenzene derivatives and related compounds **1**−**7**: nitrobenzene (**1**), 1,3-dinitrobenzene (**2**), 1,3,5-trinitrobenzene (**3**), 1,3-dinitronaphthalene (**4**), 1-methoxi-2,4,6-trinitrobenzene (**5**), 1-chloro-2,4,6-trinitrobenzene (**6**), and 1-methyl-2,4,6-trinitrobenzene (**7**) (Chart 1).

Results and Discussion

Essentially following Taylor's conditions,[12] the σ^H-complexes were prepared by the addition of nitroarene (20 mM) to a solution of Me_4NBBu_4 (from 0.05 to 0.2 M), in acetone under a nitrogen atmosphere. Initially, a large excess of tetra-*n*-butylborate anion was used to shift the equilibrium toward the σ^H-complexes.[5,11] After 2 h, a solution of DMF/0.1 M Et_4NBF_4 was added before per-

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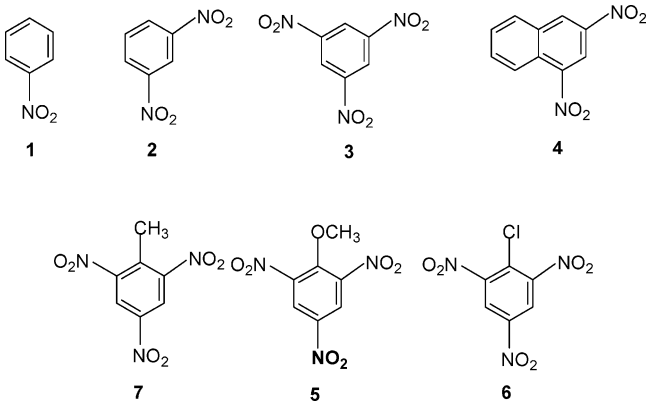
CHART 1



forming the electrochemical experiments. In the case when the nitroarene was 1,3,5-trinitrobenzene (and the acetone was removed before the addition of DMF/0.1 M Et_4NBF_4 solution), typical voltammograms are depicted in Figure 1. Figure 1a (starting with an anodic scan) and Figure 1b (starting with a cathodic scan) show the electrochemical behavior of tetrabutylborate ion and trinitrobenzene solutions that have reacted, although not completely, to form the corresponding σ^H-complex. The third cyclic voltammogram (Figure 1c) shows the electrochemical behavior of Me_4NBBu_4 in a DMF/0.1 M Et_4NBF_4 solution.

Starting with an anodic scan, the tetrabutylborate ion/σ^H-complex mixture shows two oxidation peaks. The first irreversible wave (E_{pa} = 0.35 V vs SCE) corresponds to the oxidation of Me_4NBBu_4,[11] and a second oxidation wave (E_{pa} = 0.96 V vs SCE) arises from the oxidation of the σ^H-complex (Figure 1a). In the following cathodic scan, two peaks appear at −0.53 and −0.71 V. The first corresponds to the reduction of 1,3,5-trinitrobenzene[13] to its radical anion, and the second corresponds to the reduction of the 1-butyl-2,4,6-trinitrobenzene to its radical anion. The NASH product would be formed by oxidation of the σ^H-complex during the previous anodic scan. Starting with a cathodic scan (Figure 1b), the absence of the cathodic peak at −0.71 V confirms that this peak corresponds to an oxidation product formed during the anodic scan. These results, linked with techniques of chemical analysis (see below), undoubtedly indicate that the oxidation of the σ^H-complex intermediate leads to the above-mentioned alkyl NASH product (Scheme 3)

BBu_4^- exhibits a well-defined monoelectronic oxidation wave at 0.35 V in DMF/0.1 M Et_4NBF_4 (Figure 1c). Moreover, exhaustive electroxidation experiments of BBu_4^- in ACN/0.1 M Et_4NBF_4 [14] show a charge release of 1 F, indicating the formation of *n*-Bu•. Spin electron trapping experiments on the electroxidation of organoborates have corroborated the presence of free-radical intermediates.[14,15] The oxidation is somewhat complicated depending on the solvent, through the occurrence of several consecutive reactions (Scheme 4).

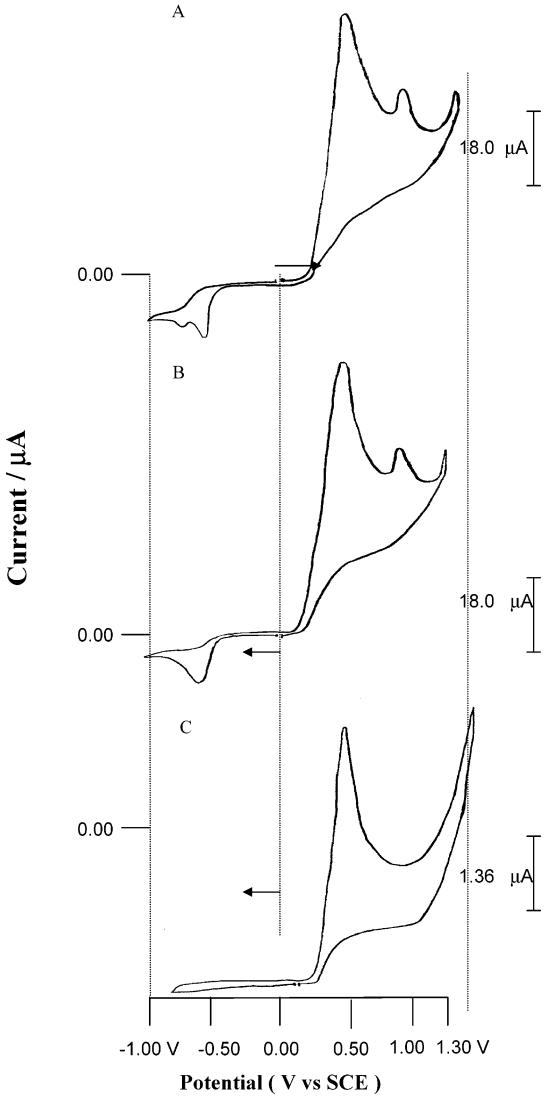
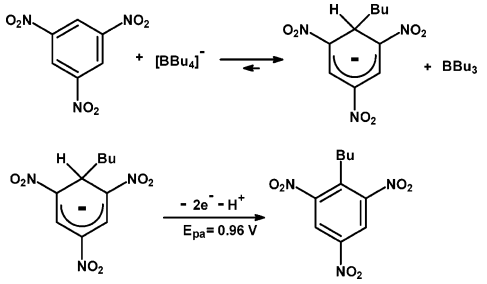


FIGURE 1. (a) Cyclic voltammetry of **3** (20 mM) + 0.1 M Me_4NBBu_4 (2 h after addition) in DMF + 0.1 M Et_4NBF_4 at 10 °C. Scan rate 1.0 V s^{-1}, glassy carbon disk electrode (0.5 mm diameter). Scan is in the potential range 0.00/1.30/−1.00/0.00. (b) Cyclic voltammetry of **3** (20 mM) + 0.1 M Me_4NBBu_4 (2 h after addition) in DMF + 0.1 M Et_4NBF_4 at 10 °C. Scan rate 1.0 V s^{-1}, glassy carbon disk electrode (0.5 mm diameter). Scan is in the potential range 0.00/−1.00/1.30/0.00. (c) Cyclic voltammetry of Me_4NBBu_4 (7.5 mM) in DMF + 0.1 M Et_4NBF_4 at 10 °C. Scan rate 1.0 V s^{-1}, glassy carbon disk electrode (0.5 mm diameter)

SCHEME 3



It was therefore advisable to ascertain the electrochemistry of tetrabutylborate ion BBu_4^- in our work

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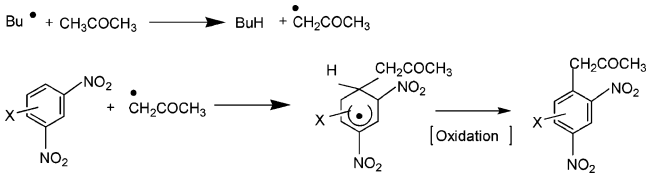
SCHEME 4

$$BBu_4^- - 1\,e^- \rightarrow BBu_4^{\bullet}$$

$$BBu_4^{\bullet} + S \rightarrow S{-}B{-}Bu_3 + Bu^{\bullet}$$

(S=Solvent)

SCHEME 5



conditions. Cyclic voltammetry and electrolysis experiments in ACN, DMF, acetone, and mixtures ACN/acetone or DMF/acetone confirm the oxidation mechanism of the BBu_4^-. BBu_4^- (in the range 0.1−0.2 M) shows a monoelectronic oxidation wave at E_{pa}, anodic peak potential, from 0.35 to 0.52 V depending on the solvent. These values are in the range of some σ^H-complexes. Thus, in certain cases, the σ^H-complex oxidation waves may be hidden inside the oxidation wave corresponding to the large excess of BBu_4^- anion. Only a shift of the anodic peak potential values indicates the presence of the σ^H-complex. An accurate determination of the oxidation potential of the σ^H-complexes can be achieved by cyclic voltammetry experiments of solutions with low molar ratio BBu_4^-/nitroarene. Furthermore, by the same technique, it is also possible to determine the percentage of nitroaromatic converted to σ^H-complex by measuring the cathodic current value corresponding to the reduction of the nitroaromatic reactant. [5,11] On the other hand, the high reactivity of *n*-Bu• radical is responsible for the presence of nondesirable products in the reaction mixture because the radical reacts with the ketone leading to the ketone radical, which attacks nitroaromatics, leading to the different substitution products (Scheme 5).

By using 1,3,5-trinitrobenzene and a 2.5-fold excess of BBu_4^- in DMF/acetone mixtures, the σ^H-complex forms in 45% yield. This complex shows an oxidation wave at 0.96 V vs SCE. After exhaustive electrolysis at 1.06 V vs SCE, 1-butyl-2,4,6-trinitrobenzene (NASH product) is obtained in 42% yield as major product and the reactant is recovered in 43% yield. 2,4,6-Trinitrobenzyl-methylcetone 5% and 1,3-dibutyl-2,4,6-trinitrobenzene 5% were obtained as the minor products. We observe that the alkyl-trinitrobenzene was obtained in excellent yield with respect to the σ^H-complex available in solution (45%); the limitation of the method therefore seems to be the relatively low amount of the σ^H-complex formed.

A second minor problem is the formation of the ketone substitution products. To avoid this problem, the acetone was removed by a continuous flow of dry nitrogen, after the reaction of nitroaromatic and the tetrabutylborate ion reaches equilibrium (ca. 2 h). The results of the electroxidation methodology carried out in acetone-free DMF solution are illustrated in Table 1. The tetrabutylborate ion/nitroarene molar ratio reported was optimized so as to obtain the best yield in the NASH product. In principle, an excess of the nucleophile favors the formation of the σ^H-complex, increasing the yield of the reaction, but overly large excess leads to the formation of dialkylated substitution product as a result of the competition between the nitroaromatic and monosubstitution product, particularly at the end of the reaction when the concentration of the unreacted nitroarene becomes low. It should be noticed that in nearly all cases the yield obtained is higher than the percent of σ-complex formed.

In summary, moderate-to-excellent yields (30−75%) were obtained with high selectivity in the monoalkyl product, since only minor amounts of disubstituted products were found in certain cases (below 15%) as a secondary product. The chemoselectivity obtained when 1-chloro-2,4,6-trinitrobenzene was used is also remarkable (Table 1, entry 6), since NASX products were not detected. Thus, the use of BBu_4^- instead of RLi or RMgX reagents provides a higher yield and a more selective synthetic route for alkylnitroderivatives.

The main limitation of the synthetic method arises from the initial thermal process, in which the concentration of σ^H-complex is determined. Following the literature,[13,16] the reaction was carried out in several solvents to test the best experimental conditions for forming the maximum amount of σ-complexes. ACN was chosen as the most appropriate solvent in order to favor their formation. Table 2 summarizes the results in this solvent.

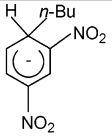
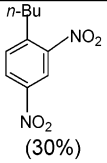
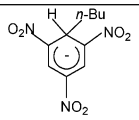
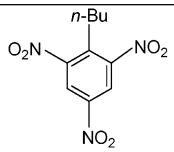
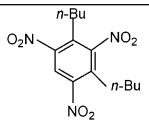
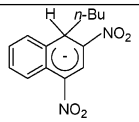
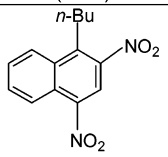
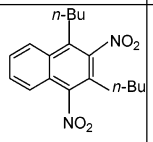
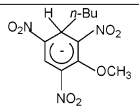
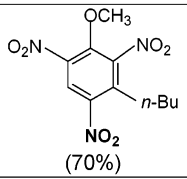
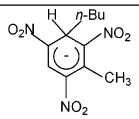
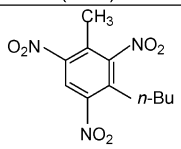
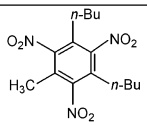
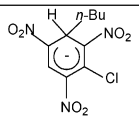
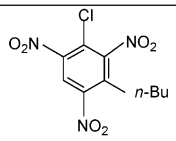
It is important to notice that in ACN the percentage of σ^H-complex formed increases considerably (more than 50% in certain cases). In the cases of 1-chloro-2,4,6-trinitrobenzene and 2,4,6-trinitrotoluene (Table 2, entries 2 and 3) the reaction is fully selective. An exception is found in the case of 1,3,5-trinitrobenzene, where a disubtituted product appears (Table 2, entry 1). However, this fact can be used to obtain the dialkylated compound in up to 36% yield, by using a large excess of BBu_4^- anion.

The NASH mechanism (Scheme 1) or S_NAr polar hydrogen mechanism requires an oxidation potential higher than that of σ^H-complexes. However, we have observed that the formation of σ-complexes increases considerably by working at potentials lower than that σ-complexes but high enough to oxidize the BBu_4^- anion. This is consistent with an alternative mechanism for this reaction. We have undertaken an electrochemical study to elucidate this mechanism and to establish its contribution to the yield of the substitution product obtained.

Cyclic voltammetry of the tetrabutylborate ion/σ^H-complex mixture shows, after electrolysis passing 0.5 F at 0.6 V vs SCE, that the oxidation peak corresponding to the tetrabutylborate ion diminishes, whereas the oxidation peak of the σ^H-complex increases considerably (Figures 2a,b vs Figure 1a,b). When the first scan is cathodic (Figure 2b), it can be observed that the quantity of unreacted 1,3,5-trinitrobenzene has diminished and in the following anodic scan the concentration of tetrabutylborate ion has been reduced to half, the concentration of the corresponding σ^H-complex having considerably increased in these conditions. Only a low amount (<10%) of NASH product is found. Similar behavior is obtained when the first scan is anodic (Figure 2a). However, in this case the oxidation of the peak at 0.96 V leads to 1-butyl-2,4,6-trinitrobenzene, as is shown by an increment of the peak current at −0.71 V during a cathodic

(16) Atkins, J.; Gold, V.; Wassef, W. R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1197.

TABLE 1. NASH in Nitroarenes by Action of BBu_4^- Anion (Acetone/DMF), via Electrochemical Oxidation

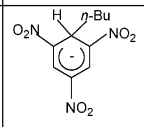
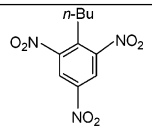
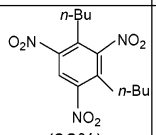
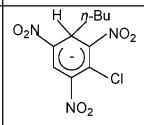
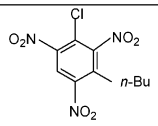
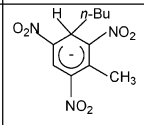
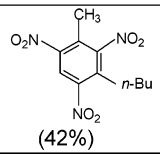
	Nitro-arene	NuH	% [a] σ-complex[b]	σ^H Complex	E_{pa} [c] (V) $\tilde{\sigma}^H$-complex	NASH Products (yields)	Minor Product (yields)	Non-reacting Starting Material Recovered
1	**2** 20mM	BBu_4^- 0.2M	15		0.44	 (30%)	-	70%
2	**3** 20mM	BBu_4^- 0.1M	45		0.96[e]	 (79%)	 (14%)	5%
3	**4** 20mM	BBu_4^- 0.1 M	30		0.50	 (75%)	 (5%)	20%
4	**5** 20mM	BBu_4^- 0.2 M	45		0.91[e]	 (70%)	-	30%
5	**6** 20mM	BBu_4^- 0.2M	35		0.89[e]	 (35%)	 (16%)	52%
6	**7** 20mM	BBu_4^- 0.2M	50		0.94[e]	 (48%)	-	52%

[a] In initial conditions before performing the coulometry. [b] The σ-complexes were carefully prepared by addition of the nucleophile to solutions of the nitroarene 20 mM in acetone under inert atmosphere (see Experimental Section). The acetone was removed before performing the coulometry. [c] Graphite working electrode. [d] The oxidation products were analyzed by cyclic voltammetry, gas chromatography/mass spectroscopy, and ^{1}H NMR. [e] Determination of characteristic E_{pa} value; the oxidation wave is not hidden inside the oxidation peak of the BBu_4^-.

scan. After consumption of 1 F at 0.6 V vs SCE (Figure 2c, first scan solid line, second scan dotted line), the results obtained are in total agreement with that previous explained. It is important to highlight that (1) the tetrabutylborate ion has practically disappeared, (2) the σ^H-complex is the major "stable" product present at the end of the process, and (3) no 1-butyl-2,4,6-trinitrobenzene (NASH product) is found as a main product (<10%) at the end of the process. After exhaustive electrolysis (2 F at 1.3 V vs SCE), Figure 2d shows two reduction waves that can be attributed to 1-butyl-2,4,6-trinitrobenzene and the dialkylated product. Scheme 6 summarizes the overall process.

The controlled potential electrolysis performed at 0.6 V leads to the formation of *n*-Bu• radicals. The *n*-Bu• radicals attack the unreacted trinitrobenzene via a radical mechanism. The resulting radical evolves, by elimination of a H^+, as a result of the C−H acidity of cyclohexadienyl radicals, leading to a nitroaromatic radical anion. This is then oxidized by the cyclohexadienyl radical (according to the standard potentials of redox couples, this is a disproportion step).[17] This reaction is

TABLE 2. NASH in Nitroarenes by Action of BBu_4^- Anion (ACN/DMF), via Electrochemical Oxidation

	Nitro-arene	NuH	% [a] σ-complex[b]		σ^H-complex	E_{pa} [c] (V) σ^H-complex	NASH Products (yields)	Minor Product (yields)	Non-reacting Starting Material Recovered
			before	after					
1	**3** 20mM	BBu_4^- 0.07M	48	85		0.96[e]	 (63%)	 (36%)	-
2	**7** 20mM	BBu_4^- 0.1 M	52			0.94[e]	 (85%)	-	29%
3	**6** 20mM	BBu_4^- 0.05M	52			0.89[e]	 (42%)	-	63%

[a] In initial conditions before performing the coulometry. [b] The σ-complexes were carefully prepared by addition of the nucleophile to solutions of the nitroarene 20 mM in ACN under inert atmosphere (see Experimental Section). The ACN was removed before to perform the coulometry. [c] Graphite working electrode. [d] The oxidation products were analyzed by cyclic voltammetry, gas chromatography/mass spectroscopy, and ^{1}H NMR. [e] Determination of characteristic E_{pa} value; the oxidation wave is not hidden inside the oxidation peak of the BBu_4^-.

similar to the termination step in the chain process $S_{RN}1$ aromatic substitution.[10,18] The final products obtained were NASH product (minor product) and the σ^H-complex (major product) (Figure 2a,b). The electrolysis experiments show the effects of the presence of *n*-Bu$^\bullet$ radicals (Table 2, entry 1), since thermal reactions yielding 48% of σ^H-complex are observed (Figure 1a,b), but after the oxidation of the BBu_4^- the percentage of σ^H-complex rises to 85% (Figure 2c). Therefore, the presence of *n*-Bu$^\bullet$ radical significantly shifts the equilibrium to the σ^H-complex. The *n*-Bu$^\bullet$ radical can also attack the NASH product, this process being more important at the end of the reaction, because the concentration of the alkylated aromatic compound is higher than that of the nitroaromatic. This fact is shown in Table 2 (entry 1), where a large percentage of dialkylated products are found (36%).

In summary, two kinds of S_NAr mechanisms operate concurrently in this reaction, a polar mechanism, more effective at adequate potentials to oxidize σ^H-complexes (and consequently to oxidize BBu_4^- anion; Table 1, entry 2) and a radical mechanism, more effective at adequate potentials to oxidize BBu_4^- anion (and not oxidizing σ^H-complexes; Table 2, entry 1). According to the results (Table 2, entry 1), the S_NAr radical mechanism can contribute in a similar way as the S_NAr polar mechanism to the overall reaction yield.

Conclusions

Performing electrochemical oxidation, alkylnitrobenzenes can be synthesized using RLi or RMgCl reagents, via the NASH and NASX mechanism, and although alkyldinitro- and trinitrobenzenes are not achieved using RLi or RMgCl reagents, these compounds can be synthesized using Me_4NBR_4 salts, via the NASH mechanism. The BR_4^- nucleophile can easily be activated by electrochemical oxidation leading to *n*-Bu$^\bullet$ radicals. This reactive species allows improvement in the yields of NASH products as well as reduction from days to hours in the time required for synthetic procedures.

Finally, a S_NAr of hydrogen polar mechanism and a S_NAr of hydrogen radical mechanism operate at the same time during the electroxidation process. The participation of each mechanism in the global product yield can thus be established.

Experimental Section

General Remarks. Electrochemical Measurements. The electrochemical cell and measurement procedures for cyclic voltammetry have previously been described.[14] All potentials are reported vs an aqueous saturated calomel electrode. A glassy carbon disk was used as the working electrode (0.5 mm diameter). Electrolyses were carried out using a PAR 273A potentiostat. A graphite rod was used as the working electrode.

Materials. 2,4,6-Trinitrotoluene (**7**) was from Union Española de Explosivos. All commercially available reactants were of the highest possible purity and were used without further purification.

(17) (a) Amatore, C.; Saveant, J. M. *J. Electroanal. Chem.* **1979**, *21*, 102. (b) Amatore, C.; Gareil, M.; Savéant, J. M. *J. Electroanal. Chem.* **1983**, *147*, 1.

(18) (a) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.***1981**, *103*, 6930. (b) Amatore, C.; Gareil, M.; Oturan, M.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Org. Chem.* **1986**, *51*, 3757.

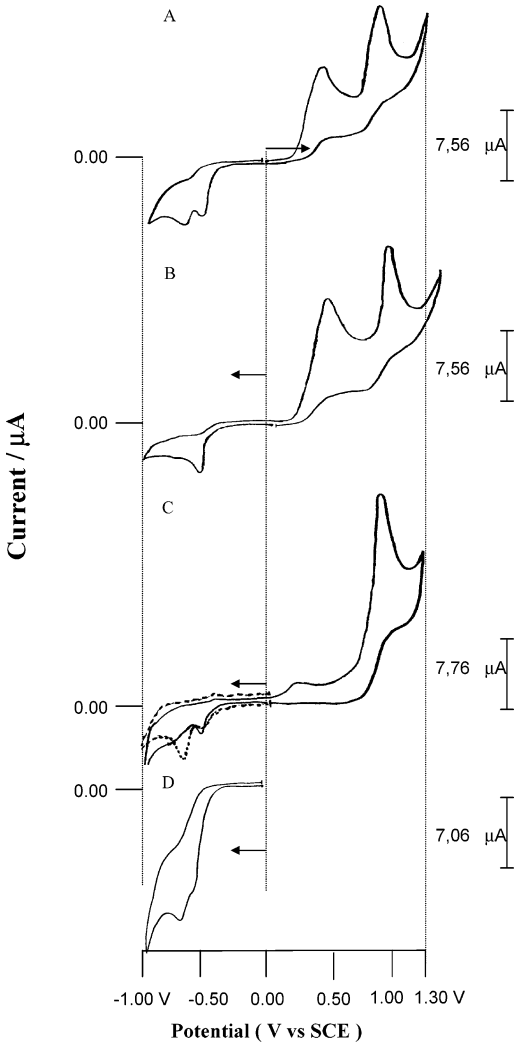
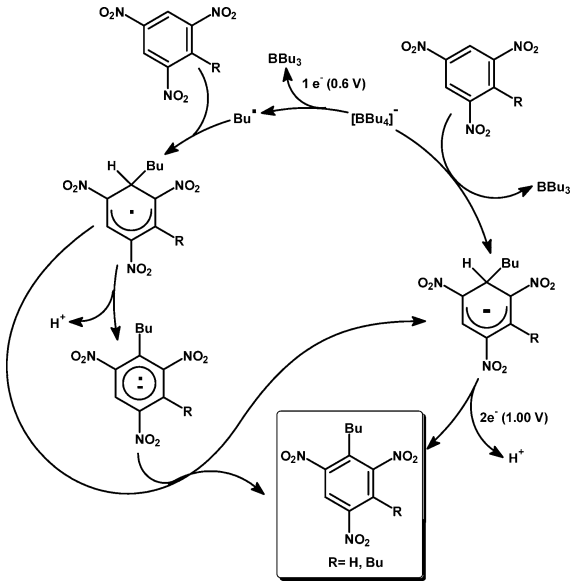


FIGURE 2. (a) Cyclic voltammetry (after electrolysis at 0.6 V vs SCE passing 0.5 F) of **3** (20 mM) + 0.1 M Me_4NBBu_4 (2 h after addition) in DMF + 0.1 M Et_4NBF_4 at 10 °C. Scan rate 1.0 V s^{-1}, glassy carbon disk electrode (0.5 mm diameter). Scan is in the potential range 0.00/1.30/−1.00/0.00. (b) Cyclic voltammetry (after electrolysis at 0.6 V vs SCE passing 0.5 F) of **3** (20 mM) + 0.1 M Me_4NBBu_4 (2 h after addition) in DMF + 0.1 M Et_4NBF_4 at 10 °C. Scan rate 1.0 V s^{-1}, glassy carbon disk electrode (0.5 mm diameter). Scan is in the potential range 0.00/−1.00/1.30/0.00. (c) Cyclic voltammetry (after electrolysis at 0.6 V vs SCE passing 1 F) of **3** (20 mM) + 0.1 M Me_4NBBu_4 (2 h after addition) in DMF + 0.1 M Et_4NBF_4 at 10 °C. Scan rate 1.0 V s^{-1}, glassy carbon disk electrode (0.5 mm diameter). Scan is in the potential range 0.00/1.30/−1.00/0.00 (dashed line) and 0.00/−1.00/1.30/0.00 (solid line). (d) Cyclic voltammetry after electrolysis at 1.3 V vs SCE passing 2 F of solution Figure 2c. Scan rate 1.0 V s^{-1}, glassy carbon disk electrode (0.5 mm diameter). Scan is in the potential range 0.00/−1.00/0.00.

Synthesis of Starting Materials. 1-Methoxy-2,4,6-trinitrobenzene (**5**) and 1-chloro-2,4,6-trinitrobenzene (**6**) were synthesized, following described procedures.[20,21]

SCHEME 6



General Procedure for NASH Described in Table 1. A solution of tetramethylammonium tetrabutylborate (Me_4NBBu_4) (0.1, 0.2 M in acetone, 1 mL) prepared under nitrogen atmosphere was added to a solution of the nitroarene (20 mM) in acetone (2 mL) also kept under a nitrogen atmosphere. The corresponding σ^H-complex was prepared by careful addition of the nucleophile to the solution of the nitroarene. After 2 h, the acetone was removed by passing a dry nitrogen flow through the reaction mixture.

General Procedure for NASH Described in Table 2. A solution of tetramethylammonium tetrabutylborate (Me_4NBBu_4) (0.05−0.1 M in ACN (1 mL)) prepared under a nitrogen atmosphere was added to a solution of the nitroarene (20 mM) in ACN (2 mL) also kept under a nitrogen atmosphere. The corresponding σ^H-complex was prepared by careful addition of the nucleophile to the solution of the nitroarene. After 2 h, the ACN was removed by passing dry nitrogen flow through the reaction mixture.

General Electrochemical Procedure for NASH Described in Tables 1 and 2. A 0.10 g portion of Et_4NBF_4 dissolved in 5 mL of DMF was added to the solid residue obtained after the evaporation of acetone or ACN. The oxidation peak potentials of the σ^H-complexes were measured by cyclic voltammetry. Electrolysis was then carried out at potentials ca. 100 mV more positive than the value measured for each σ^H-complex, using a graphite rod as a working electrode.

The electrolysis was then stopped when the current intensity dropped to nearly 0. The reaction mixture was dissolved in toluene and extracted with water. The organic layer was dried with Na_2SO_4, and the solvents were evaporated to leave a residue that was analyzed by gas chromatography. The final products were analyzed by gas chromatography/mass spectrometry, ^{1}H NMR, and cyclic voltammetry. Product yields were calculated by gas chromatography and cyclic voltammetry, after verifying from the ^{1}H NMR spectrum of the crude product that only the substitution products and starting material were present.

Reaction Products. 4-Butyl-1,3-dinitrobenzene.[22] (Table 1, entry 1) ^{1}H NMR (250 MHZ, CD_3CN) δ 8.67 (d, J = 2.33 Hz, 1H, Ar−H), 8.54 (dd, J = 8.16, J = 2.33 Hz, 1H, Ar−H), 7.75 (d, J = 8.16 Hz, 1H, Ar−H), 2.75 (t, 2H, $-CH_2$), 1.64−1.71 (m, 2H, $-CH_2$), 1.34−1.40 (m, 2H, $-CH_2$), 0.93 (t, 3H, $-CH_3$); MS (70 eV) *m*/*z* (%) 224 (1) $[M]^+$, 207 (9), 190 (26), 175 (12), 164 (95), 161 (35), 146 (35), 143 (30), 118 (27), 115 (28),

(19) Andrieux, C. P.; Larrumbre, D.; Gallardo, I. *J. Electroanal. Chem*. **1991**, *304*, 241.
(20) Reese, C. B.; Pei-Zhuo, Z. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2291.
(21) Lam, K.-B.; Miller, J.; Samenho, P. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 457.
(22) Zou, G.; Falck, J. R. *Tetrahedron Lett.* **2001**, *42*, 5817.

91 (36), 77 (43), 57 (22), 43 (100); MS (NCI, CH_4) 224 (M^-, 100), 225 (12), 195 (M^- − NO, 3), 176 (M^- − NO − NO, 91).

2-Butyl-1,3,5-trinitrobenzene.[12,23,24] (Table 1, entry 2, Table 2, entry 1) ^{1}H NMR (250 MHZ, CD_3CN) δ 8.84 (s, 2H, Ar−H), 3.62 (t, J = 7.75 Hz, 2H, $-CH_2$), 1.53−1.75 (m, 2H, $-CH_2$), 1.30−1.50 (m, 2H, $-CH_2$), 0.93 (t, 3H, $-CH_3$); MS (70 eV) m/z (%) − $[M]^+$, 253 (3), 252 (33), 235 (8), 210 (29), 178 (6), 163 (5), 89 (20), 77 (23), 76 (26), 57 (30), 43 (100); MS (NCI, CH_4) 269 (M^-, 100), 270 (M^- + 1, 13), 239 (M^- − NO, 78), 209 (M^- − NO − NO, 65).

1-Butyl-2,4-dinitronaphthalene.[25] (Table 1, entry 3) ^{1}H NMR (250 MHZ, CD_3CN) δ 9.19 (d, J = 0.95 Hz, 1H, Ar−H), 8.45 (dd, J = 7.50, J = 1.35 Hz, 1H, Ar−H), 7.99 (m, J = 8.50 Hz, J = 6.85 Hz, J = 0.85 Hz, 1H, Ar−H), 7.74 (m, J = 8.50 Hz, J = 1.35 Hz, 1H, Ar−H), 7,57 (m, J = 7.50, J = 6.85 Hz, J = 1.35 Hz, 1H, Ar−H), 3.45 (t, 2H, $-CH_2$), 1.43−1.68 (m, 2H, $-CH_2$), 1.29−1.42 (m, 2H, $-CH_2$), 0.96 (t, 3H, $-CH_3$); MS (70 eV) m/z (%) 274 (35) $[M]^+$, 275 (6), 228 (4), 201 (4), 196 (8), 185 (21), 196 (26), 157 (13), 140 (50), 139 (71), 128 (43), 115 (38), 101 (13), 89 (14), 71 (22), 57 (8), 43 (72), 41 (33).

2-Butyl-4-methoxy-1,3,5-trinitrobenzene.[25] (Table 1, entry 4) ^{1}H NMR (250 MHZ, CD_3CN) δ 8.95 (s, 1H, Ar−H), 4.06 (s, 3H, $-OCH_3$), 3.51 (t, J = 6.50 Hz, 2H, $-CH_2$), 1.53−1.73 (m, 2H, $-CH_2$), 1.29−1.51 (m, 2H, $-CH_2$), 0.97 (t, 3H, $-CH_3$); MS (70 eV) m/z (%) 299 (2) $[M]^+$, 282 (46), 249 (5), 223 (5), 174 (3), 147 (4), 77 (21), 57 (24), 43 (100).

2-Butyl-4-methyl-1,3,5-trinitrobenzene.[26] (Table 1, entry 5 and Table 2, entry 3) ^{1}H NMR (250 MHZ, CD_3CN) δ 8.75 (s, 1H, Ar−H), 3.48 (t, J = 6.35 Hz, 2H, $-CH_2$), 2.36 (s, 3H, Ar−CH_3), 1.65−1.75 (m, 2H, $-CH_2$), 1.38−1.50 (m, 2H, $-CH_2$), 0.93 (t, J = 7.19 Hz, 3H, $-CH_3$); MS (70 eV) m/z (%) 283 (2) $[M]^+$, 266 (25), 267 (4), 223 (25), 214 (2), 194 (4), 148 (7), 128 815), 115 (20), 103 (12), 90 (14), 89 (15), 78 (12), 77 (29), 57 (21), 43 (100).

3-Butyl-1-chloro-2,4,6-trinitrobenzene.[27−29] (Table 1, entry 6 and Table 2, entry 2) ^{1}H NMR (250 MHZ, CD_3CN) δ 8.75 (s, 1H, Ar−H), 3.58 (t, J = 6.35 Hz, 2H, $-CH_2$), 1.52−1.75 (m, 2H, $-CH_2$), 1.30−1.50 (m, 2H, $-CH_2$), 0.93 (t, J = 7.19 Hz, 3H, $-CH_3$); MS (70 eV) m/z (%) 303 (1) $[M]^+$, 304 (0.3), 285 (18), 244 (16), 213 (5), 168 (1), 99 (11), 87 (16), 75 (23), 74 (11), 59 (14), 57 (21), 43 (100).

2,4-Dibutyl-1,3,5-trinitrobenzene.[30−32] (Table 1, entry 2; Table 2, entry 1) ^{1}H NMR (250 MHZ, CD_3CN) δ 8.77 (s, 1H, Ar−H), 3.60 (m, 4H, $-CH_2$), 1.60−1.80 (m, 4H, $-CH_2$), 1.35−1.55 (m, 4H, $-CH_2$), 0.93 (m, 6H, $-CH_3$); MS (70 eV) m/z (%) 325 (4) $[M]^+$, 309 (4), 237 (10), 210 (2), 128 (15), 115 (20), 91 (14), 89 (12), 77 (18), 71 (14), 63 (12), 57 (26), 43 (100); MS-(NCI, CH_4) 325 (M^-, 100), 326 (M^- + 1, 17), 295 (M^- − NO, 13).

Subproducts Obtained (1−15%). 1,3-Dibutyl-2,4-dinitronaphthalene. (Table 1, entry 3) This product could not be isolated and was therefore tentatively assigned by GC/MS spectroscopy. MS (70 eV) m/z (%) 330 (49) $[M]^+$, 331 (5), 253 (12), 242 (15), 197 (14), 154 (22), 152 (32), 141 (27), 127 (26), 115 (30), 57 (10), 43 (100).

2,4-Dibutyl-6-methyl-1,3,5-trinitrobenzene.[31−33] (Table 1, entry 5) This product could not be isolated and was therefore tentatively assigned by GC/MS spectroscopy. MS (70 eV) m/z (%) 339 (5) $[M]^+$, 323 (6), 322 (30), 280 (7), 266 (18), 210 (12), 143 (10), 128 (22), 115 (31), 91 (21), 57 (100), 43 (95), 41 (96).

2,4-Dinitrophenyl-acetone.[5] ^{1}H NMR (250 MHz, CD_3CN) δ 8.98 (d, J = 2.50 Hz, 1H), 8.45 (dd, J = 8.45 Hz and J = 2.50 Hz, 1H), 7.65 (d, J = 8.45 Hz, 1H), 4.41 (s, 2H), 2.29 (s, 3H)

2,4,6-Trinitrophenyl-acetone.[11] ^{1}H NMR (250 MHz, CD_3CN) δ 8.95 (s, 2H), 4.49 (s, 2H), 2.23 (s, 3H).

2,4-Dinitronaphthyl-acetone.[14] ^{1}H NMR (250 MHz, CD_3CN) δ 8.61 (s, 1H), 8.10 (d, J = 3.84 Hz, 1H), 8.10 (d, J = 3.84 Hz, 1H), 8.04 (m, 1H), 7.79 (d, J = 7.37 Hz, 1H), 7.71 (m, 1H), 4.04 (s, 2H), 2.12 (s, 3H).

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