Electrochemical Synthesis of Nitroaromatic Ketones[‡]

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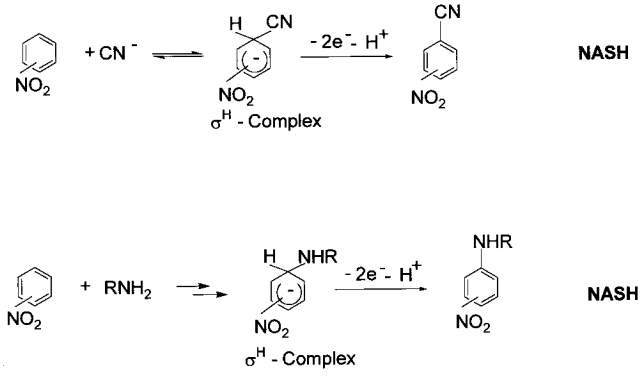
Nitroaromatic ketones are readily prepared by nucleophilic aromatic substitution of hydrogen in nitroarenes by electrochemical oxidation. Carbanions of various ketones were added to selected nitroarenes in DMF/ketone mixtures leading to formation of the σ^H complexes. The reaction was promoted using potassium *tert*-butoxide as a base. Useful yields were achieved (80–100%) in the *C*-arylation of ketones. In most cases, the process proceeded with high selectivity. This new method represents an environmentally favourable route for obtaining nitroaromatic ketones.

Introduction

The preceding paper[1] describes the synthesis of nitroanilines by means of a new electrochemically promoted nucleophilic aromatic substitution of hydrogen (Scheme 1).[2] These reactions represent a significant improvement on previously described methods due to the control that electrochemistry allows over the chemo- and regioselectivity. In our continuing effort to extend this methodology, we describe herein the electrochemical nitroarylation of ketones.



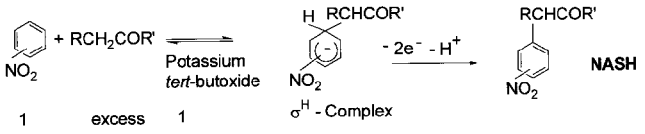
Scheme 1

Only very few examples of S_NAr^H reactions on nitroaromatic compounds using anions derived from ketones as nucleophiles can be found in the literature, and these are largely restricted to the peculiar reactivity of *para*-chloronitrobenzene.[3] However, we have very recently described the direct coupling of various nucleophiles, including ketones, with nitroaromatic compounds by means of an oxidative ($KMnO_4$) S_NAr^H reaction promoted by fluoride ions, in yields that range from 29 to 49% in the case of ketones.[4] A photochemical alternative, that despite giving reasonable yields of nitroaromatic ketones needs special conditions to achieve good reproducibility, was also recently reported by one of us.[5] Interestingly, as far as we are aware, there has been no report of direct hydrogen substitution in nitrobenzene by ketone-derived anions in preparatively useful yields.

The best alternative to the S_NAr^H reaction is vicarious nucleophilic substitution.[6a] This reaction allows the synthesis of nitroaromatic ketones, but fails with nitrobenzene as a substrate (low electrophilicity), and in any case the need for an auxiliary leaving group still remains.[7a–7c]

In a recent paper,[7d] the first unambiguous observation of enolate *O*-adduct formation with 1,3,5-trinitrobenzene was reported. This may occur under suitable conditions, e.g. at −50 °C in an acetonitrile/dimethoxyethane mixture. The author further demonstrated that on increasing the temperature to 20 °C the *O*-adduct was converted to the *C*-adduct, which remained stable in the solution for several days.

We describe herein that by using a strong base (in order to shift the first equilibrium to the right; Scheme 2), and electrochemical oxidation of the σ^H complex intermediate at a controlled potential, a variety of nitroaromatic ketones, including mononitrophenyl ketones, can be synthesized in good preparative yields.



Scheme 2

[‡] Electrochemically Promoted Nucleophilic Aromatic Substitution of Hydrogen, II. − Part I: Ref.[1]

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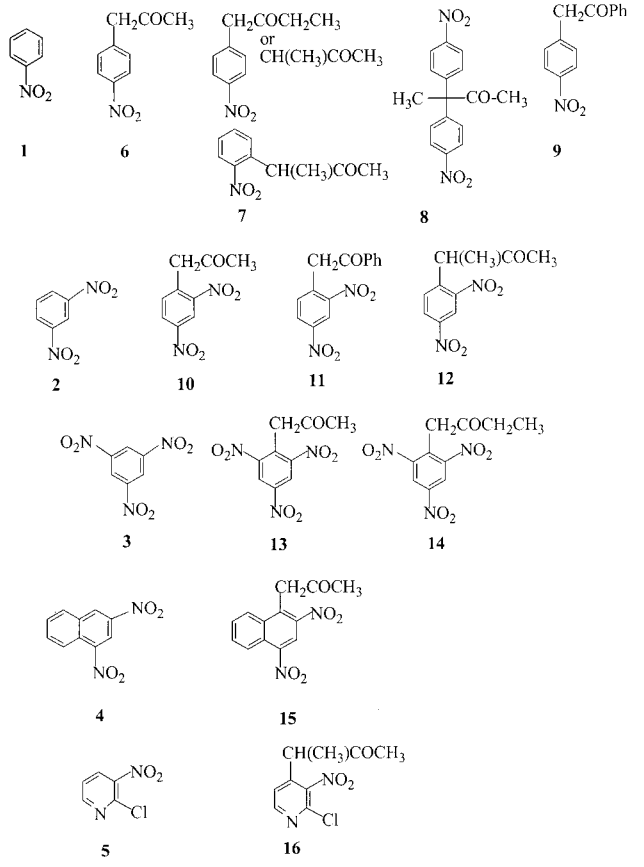
Results and Discussion

In order to establish the synthetic scope of the electrochemical method, this study has been carried out with a wide series of nitrobenzene derivatives and related compounds: nitrobenzene (**1**), 1,3-dinitrobenzene (**2**), 1,3,5-trinitrobenzene (**3**), 1,3-dinitronaphthalene (**4**), and 2-chloro-3-nitropyridine (**5**) (see Scheme 3). Moreover, different ketones were used (acetone, 2-butanone, and acetophenone). The base used to deprotonate the various ketones and to promote the nucleophilic attack was the same in all the cases, namely potassium *tert*-butoxide.



Scheme 3

The mechanism of chemical and electrochemical oxidation of σ^H complexes has been widely studied in our laboratory.[1,5] In this work, we adapted the best experimental conditions to achieve high yields and a selective synthesis.

First of all, a solution of the nitroaromatic compound was prepared under nitrogen in a large excess of ketone. Potassium *tert*-butoxide was then added slowly and carefully, as uniformly as possible. The mixture was kept under nitrogen. This procedure aims to favour: (a) stoichiometric formation of the most stable ketone carbanion present in the reaction mixture, and (b) fast and quantitative nucleophilic attack by the corresponding ketone carbanion.

However, a ketone is not an appropriate solvent for carrying out electrochemical experiments. Therefore, a solution of the supporting electrolyte in DMF was prepared under nitrogen. This DMF solution was then carefully added to the nitroaromatic solution under nitrogen. These experimental conditions allow us to obtain a high and selective concentration of the σ^H complex and are appropriate for carrying out electrochemical experiments. Cyclic voltammetry experiments (Figure 1) and controlled potential electrolysis (Table 1) allow us to describe the formation of σ^H complexes and to obtain the corresponding NASH product.

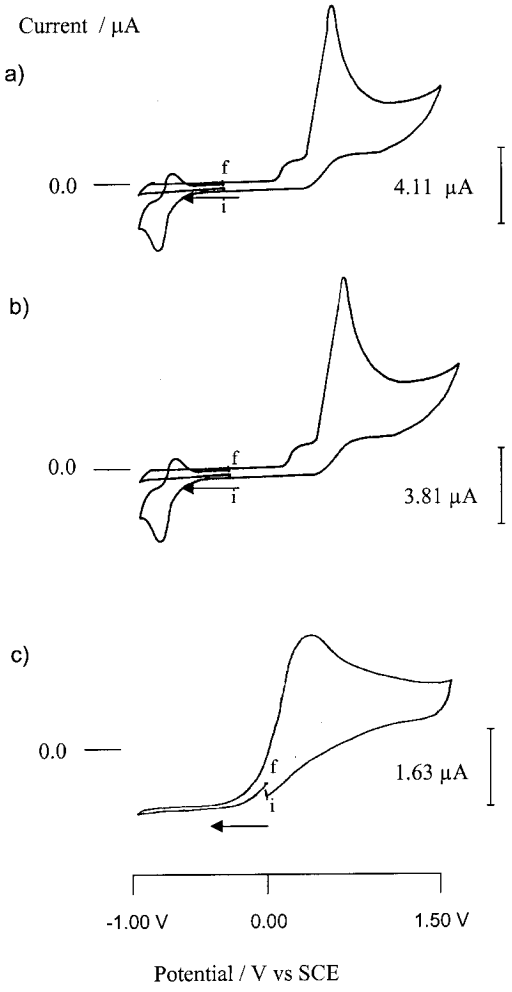


Figure 1. (a) Cyclic voltammetry of a mixture of **2** (10.0 mM) and butanone in the presence of *t*BuOK in DMF + 0.1 M nBu_4NBF_4 at 10 °C; scan rate 1.0 $V{\cdot}s^{-1}$, glassy carbon disc electrode (0.05 mm diameter); the scan is in the potential range: −0.50/−1.00/1.50/−0.50 V (2 cycles); (b) cyclic voltammetry of a mixture of **2** (10.0 mM) and butanone in the presence of *t*BuOK in DMF + 0.1 M nBu_4NBF_4 under an inert gas at 10 °C; scan rate 1.0 $V{\cdot}s^{-1}$, glassy carbon disc electrode (0.05 mm diameter); the scan is in the potential range: −0.50/−1.00/1.50/−0.50 V (2 cycles); (c) cyclic voltammetry of the acetone enolate formed from a mixture (blank reaction) of acetone (3 mL) + 10.0 mM *t*BuOK in DMF (3 mL) + 0.1 M nBu_4NBF_4 at 10 °C; scan rate 0.7 Vs^{-1}, glassy carbon disc electrode (0.05 mm diameter); the scan is in the potential range: 0.00/1.50/−1.00/0.00 V

The first two voltammograms, Figure 1a and b, show the electrochemical behaviour of **2**/ketone/*t*BuOK mixtures, where the ketones used are acetone and 2-butanone, respectively. On the first cathodic scan, no reduction waves

are observed, indicating that no nitroaromatic compounds are present in the mixture (100% σ complex; 100% nucleophilic attack), while an irreversible two-electron oxidation wave appears at 0.47 and 0.51 V, respectively. On the second reduction scan, a reduction wave appears (at ca. −0.88 V), which corresponds to the NASH product formed as a result of the first anodic process (**10** and **11**, respectively).

Figure 1c shows a blank experiment. A ketone/*t*BuOK/DMF/0.1 M nBu_4NBF_4 mixture shows the presence of an irreversible one-electron wave at 0.20 V. Similar experiments have been reported in the literature;[6b] the same potential values were obtained for the same enolate anions, hence the peak at 0.20 V corresponds to oxidation of the enolate anion. Note that the two voltammograms (Figure 1a and b) show a previous oxidation peak at 0.20 V. Thus, we conclude that this previous peak corresponds to enolate oxidation.

In Table 1, the results of the electrochemically promoted S_NAr of hydrogen are presented. The σ^H complexes (column 5) were prepared by the careful addition of potassium

Table 1. Electrolyses (2 F/mol) of the σ^H complexes (at oxidation peak potential plus ca. 100 mV) obtained by reactions of the nitroaromatic compounds with ketones in the presence of potassium *tert*-butoxide[a] at 10 °C

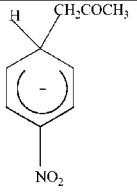
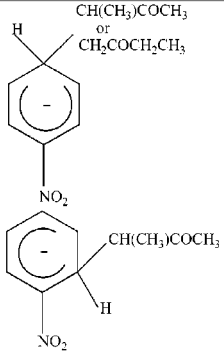
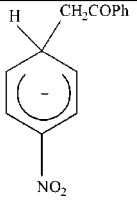
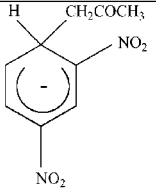
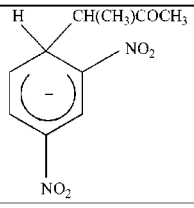
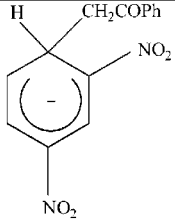
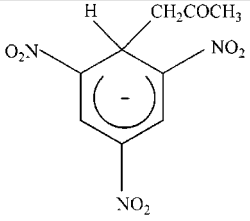
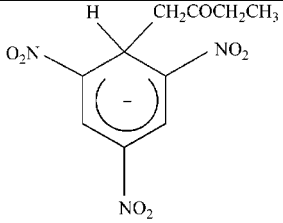
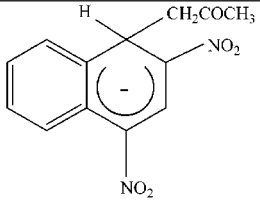
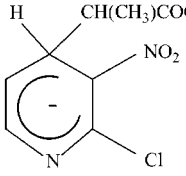
Entries	Reactant[a]	Solvent		% σ^H-Complexes	σ^H-Complex	E_{pa} (V) σ^H-Complex ($1.0\ Vs^{-1}$)	NASH product	Yield[b] (%)
		DMF (ml)	Nucleophile (ml)					
1	nitrobenzene	3 ml	acetone (3 ml)	50 %		0.38 broad	**6**	80 %
2	nitrobenzene	3 ml	2-butanone (3 ml)	80 %		0.07 0.03	**7**	60 % 20 %
3	nitrobenzene	3 ml	acetophenone (1.5 ml)	100 %		0.05	**9**	90 %
4	1,3-dinitro-benzene	3 ml	acetone (3 ml)	100 %		0.47	**10**	90 %
5	1,3-dinitro-benzene	3 ml	2-butanone (3 ml)	95%		0.51	**11**	91 %

Table 1. *(Continued)*

Entries	Reactant[a]	Solvent		% σ^H-Complexes	σ^H-Complex	E_{pa} (V) σ^H-Complex (1.0 Vs^{-1})	NASH product	Yield[b] (%)
		DMF (ml)	Nucleophile (ml)					
6	1,3-dinitro-benzene	3 ml	acetophenone (1.5 ml)	85%		0.56	**12**	85 %
7	1,3,5-trinitro-benzene	3 ml	acetone (3 ml)	70		0.91	**13**	60 %
8	1,3,5-trinitro-benzene	3 ml	2-butanone (3 ml)	80		0.91	**14**	70 %
9	1,3-dinitro-naphthalene	3 ml	acetone (3ml)	70		0.48	**15**	80 %
10	2-chloro-3-nitropyridine	3 ml	2-butanone (3 ml)	80		0.55	**16**	60 % (57 %)[c]

[a] Molar ratio substrate/potassium *tert*-butoxide = 1:1. [b] The NASH products were analysed by cyclic voltammetry, gas chromatography, ^1H NMR, and ^{13}C NMR (see Exp. Sect.). [c] Preparative yield and data for the new compound are presented in the Exp. Sect.

tert-butoxide to nitroarene solutions. The solutions were prepared under nitrogen as described previously using DMF/ketone mixtures as the solvent. The species present were characterized by cyclic voltammetry (column 6). The percentage of nucleophilic attack (% σ^H complex, column 4) was also determined by means of cyclic voltammetry. Note that the reactions proceed with high selectivity. Only in Entry 2 is a mixture of products obtained.

In Entry 1, the preparation of 4-nitrophenylacetone (**6**) is described. Cyclic voltammetry experiments performed prior to the electrolysis indicated that the extent of nucleophilic attack was only about 50%. By the addition of an extra 0.5 equiv. of potassium *tert*-butoxide, it was possible to increase the product yield by shifting the equilibrium (Scheme 2) to the right. The excess potassium *tert*-butoxide (potassium *tert*-butoxide is stable in DMF solution and gives rise to an oxidation wave at ca. 1.33 V) present in the mixture has another function; in addition to deprotonating the ketone, it also reacts with the protons formed in the electrochemical oxidation of the σ^H complex (a proton per mol is lost; Scheme 2). The same procedure was applied for 1,3-dinitronaphthalene (**4**, Entry 9), and the same phenomenon was observed in the preparation of 2,4-dinitronaphthylacetone (**15**).

In the case of Entry 2, using an excess of potassium *tert*-butoxide (2.5 mol), we obtained the disubstituted product 3,3-bis(4-nitrophenyl)-2-butanone (**8**) in a selective manner. In this experiment (Entry 2), a mixture of products was obtained, in contrast to the high selectivity observed in all

other cases. This may have been due to the way in which the base was added (too rapidly), since only a very slow addition leads to the thermodynamically more stable anions and to selective processes. Three oxidation products were identified: 1-(4-nitrophenyl)-2-butanone (**7c**) and 3-(4-nitrophenyl)-2-butanone (**7a**) (yield of *para* substitution products 60%), and 3-(2-nitrophenyl)-2-butanone (**7b**) (yield of *ortho* substitution product 20%).

In Entry 3, the corresponding reaction with acetophenone is described. This reaction affords 4-nitrophenylacetophenone (**9**) in excellent yield.

In general, the reaction site is determined by the nitro group, which directs the substitution to the *ortho* and *para* positions. In Entries 1, 3, and 4, the NASH occurs selectively at the *para* position of nitrobenzene. This general substitution pattern arises from the most stable σ^H complex, which predominates in the solution.

The results achieved using different nitroaromatic compounds [1,3-dinitrobenzene (**2**) and 1,3,5-trinitrobenzene (**3**)] are presented in Entries 4−8. The yields obtained for *C*-arylation are close to 90%. In the case of 1-(2,4-dinitrophenyl)acetone (**10**), a yield of 90% was obtained (Entry 4), this being significantly higher than that reported in the literature for the corresponding VNS reaction using chloroacetone (68%),[7a] and in our case there is no requirement for an auxiliary leaving group. We would like to comment on the high selectivity of the process and the excellent yields obtained. The reaction site is determined by the nitro groups, which direct the substitution exclusively to the *ortho* or *para* positions. In the case of 1,3-dinitrobenzene (**2**), the NASH occurs selectively at the 1-position. It seems to be a general process (Entries 4−6). In Entries 4−6, no starting material could be detected at the end of the reactions. In Entries 7 and 8, we could recover some unreacted starting material.

It is significant that in Entry 5 the only product obtained was 3-(2,4-dinitrophenyl)-2-butanone (**11**). This confirms that we are operating under thermodynamic conditions since a simple retroanalysis indicates that the reaction takes place with the more stable enolate and that the oxidation takes place on the more stable σ complex.

The reactivity of 1,3,5-trinitrobenzene is described in Entries 7 and 8, in which only one product was formed. Note that when butanone was used as the nucleophile (Entry 8), the product formed was 1-(2,4,6-trinitrophenyl)-2-butanone (**14**). Thus, in this case, the final product formed was that obtained via the primary carbanion, which can probably be attributed to steric effects.

In the case of 1,3,5-trinitrobenzene (Entries 7 and 8), it is known that the initial formation of the *C*-centred enolate adduct may lead to the formation of a bicyclic compound under certain experimental conditions.[7b,7c] In this work, no bicyclic compounds were found. The experimental conditions were chosen in order to obtain a high yield of the σ^H complex.

Using 1,3-dinitronaphthalene as the substrate (Entry 9), the synthesis was directed by the two nitro groups to selectively afford 2,4-dinitronaphthylacetone (**15**).

The case of 2-chloro-3-nitropyridine (**5**) is of special interest (Entry 10) since no substitution of the chloro substituent (*ipso* substitution) was found. Thus, the only product formed was 3-(2-chloro-3-nitro-4-pyridyl)-2-butanone (**16**). Furthermore, the unreacted starting material could easily be recovered.

Finally, in Table 2, a comparison between chemical[4] and electrochemical oxidation is presented. The yields obtained electrochemically are seen to be rather better. Moreover, the electrochemical technique also offers a route to new products that could not have been obtained by NASH reactions using chemical oxidants, for instance compound **15**.

Conclusion

NASH becomes a versatile tool in synthetic transformations of electrophilic arenes when an electrochemical oxidation step is performed. It allows the direct introduction of

Table 2. Chemical[4] vs. electrochemical oxidation

Entry	Nitroarene + base (nitroarene/base)	Solvent (NuH or NuH/DMF mixture)	Time	Type of oxidation chemical $KMnO_4$	electro-chemical	E_{pa} [V] σ^H complex	NASH product (yield)
1	**2** + FTBA·$3H_2O$ (1:5)	acetone	20 min	Yes		0.47	**10** (42%)
2	**2** + *t*BuOK (1:1)	acetone/DMF	1.5 h		Yes	0.47	**10** (91%)
3	**2** + FTBA·$3H_2O$ (1:5)	2- butanone	1 h	Yes		0.51	**12** (44%)
4	**2** + *t*BuOK (1:1)	2- butanone/DMF	1.5 h		Yes	0.51	**12** (90%)
5	**4** + FTBA·$3H_2O$ (1:5)	acetone	1.5 h	Yes		0.48	[a]
6	**4** + *t*BuOK (1:1)	acetone/DMF	1.5 h		Yes	0.48	**15** (80%)

[a] Extensive degradation of the reaction mixture was observed.

a variety of functionalized carbon substituents and provides access to many synthetically useful intermediates.

The use of electrochemical techniques to oxidize the σ^H complexes allows the selection of the oxidation potential that is required in each case. In this way, more selective oxidations can be achieved and more positive potentials can be applied than by using chemical oxidizing agents. Moreover, the use of a clean technology permits the recovery of the unreacted starting material.

Experimental Section

General Remarks

Electrochemical Measurements: The electrochemical cell and measurement procedures for cyclic voltammetry have been described previously.[8] All the potentials are reported vs. an aqueous saturated calomel electrode. A glassy carbon disc was used as the working electrode (0.05 mm diameter). Electrolyses were carried out using a PAR 273A potentiostat. A graphite rod was used as the working electrode.

Materials: DMF (SDS, "pour syntheses peptidiques") and nBu$_4$NBF$_4$ (Fluka, puriss.) were used without purification. Nitrobenzene (**1**), 1,3-dinitrobenzene (**2**), and 1,3-dinitronaphthalene (**4**) were purchased from Aldrich; 1,3,5-trinitrobenzene (**3**) was from Supelco; 2-chloro-3-nitropyridine (**5**) was from Acros Organics; potassium *tert*-butoxide was from Aldrich. All the commercially available reactants were of high purity and were used without purification.

General Procedure for NASH in Nitroarenes: A solution of the nitroarene (20 mM) in a DMF/ketone mixture (6 mL), which contained 0.1 M NBu$_4$BF$_4$ (0.1646 g) as a supporting electrolyte, was prepared under nitrogen. The corresponding σ^H complex was prepared by the slow and careful addition of *tert*-butoxide (nitroarene/base ratio 1:1, 1:1+0.5, 1:2, depending on the individual case; see text) to the solution of the nitroarene under nitrogen. The oxidation peaks of the σ^H complexes were measured by cyclic voltammetry. Electrolyses were then carried out at potentials ca. 100 mV more positive that the value measured for each σ^H complex, using a graphite rod as the working electrode. After the passage of 2 F/mol (calculated on the basis of the initial concentration of the σ^H complexes), the electrolysis was stopped and the mixture was subsequently partitioned between water and toluene. The organic layer was dried with Na_2SO_4, the solvents were evaporated, and the residue was analysed by gas chromatography and ^{1}H NMR. The analysis showed the presence of nitro compounds. The final products were analysed by gas chromatography, ^{1}H NMR, ^{13}C NMR, and cyclic voltammetry and were identified by comparison of their spectroscopic properties with those reported in the literature. The yields were not optimized and were calculated by gas chromatography and ^{1}H NMR of the crude products. When acetophenone was used as the ketone, the residue was distilled under reduced pressure through a short fractionating column (b.p. 85 °C/8 Torr; b.p. at atmospheric pressure 201 °C) in order to eliminate the excess ketone present in the mixture.

Typical Procedure for Preparative Electrolysis. − Generation of 3-(2-Chloro-3-nitro-4-pyridyl)-2-butanone (11) by Preparative Electrolysis: A solution of the nitroarene (50 mg of 2-chloro-3-nitropyridine) in 2-butanone (5 mL) was prepared under nitrogen. Potassium *tert*-butoxide (1.2 equiv.) was then carefully added. The mixture was then kept under nitrogen, and an electrolyte solution of NEt_4BF_4 (0.2171 g) in DMF (5 mL) was added carefully. The crude product [or mixture of product(s) and reactants] was purified or separated by chromatography on silica gel eluting with chloroform. 3-(2-Chloro-3-nitro-4-pyridyl)-2-butanone (**11**)was obtained as the sole product (40 mg, 57%), besides 40% (20 mg) of recovered unreacted starting material, 2-chloro-3-nitropyridine.

1-(4-Nitrophenyl)acetone (6):[9] Table 1, Entry 1. ^{1}H NMR (250 MHz, CD_3CN): δ = 7.89 (d, J = 8.38 Hz, 2 H), 7.34 (d, J = 8.38 Hz, 2 H), 3.59 (s, 2 H), 2.42 (s, 3 H). ^{13}C NMR (60 MHz, CD_3CN): δ = 25.56, 58.50, 128.02, 128.92, 148.05, 155.05, 198.05.

3-(4-Nitrophenyl)-2-butanone (7a):[10] Table 1, Entry 2. ^{1}H NMR (250 MHz, CD_3CN): δ = 8.33 (d, J = 9.03 Hz, 2 H), 8.17 (d, J = 9.03 Hz, 2 H), 3.82 (q, J = 7.17 Hz, 1 H), 2.42 (s, 3 H), 1.30 (dd, J = 7.17 Hz, 3 H).

3-(2-Nitrophenyl)-2-butanone (7b):[11] Table 1, Entry 2. ^{1}H NMR (250 MHz, CD_3CN): δ = 7.57 (m, 1 H), 7.55 (m, 1 H), 7.51 (m, 1 H), 7.19 (dd, J = 6.53, J = 2.18 Hz, 1 H), 2.39 (s, 3 H), 1.55 (dd, J = 7.18 Hz, 3 H).

1-(4-Nitrophenyl)-2-butanone (7c):[12] Table 1, Entry 2. ^{1}H NMR (250 MHz, CD_3CN): δ = 7.89 (d, J = 8.53 Hz, 2 H), 7.47 (d, J = 8.53 Hz, 2 H), 3.60 (s, J = 7.17 Hz, 2 H), 2.67 (q, J = 7.2 Hz, 2 H), 1.12 (t, J = 7.2 Hz, 3 H).

3,3-Bis(4-nitrophenyl)-2-butanone (8):[13] Table 1, Entry 2. ^{1}H NMR (250 MHz, CD_3CN): δ = 7.84 (d, J = 8.20 Hz, 2 H), 7.28 (d, J = 8.20 Hz, 2 H), 2.51 (s, 3 H), 2.38 (s, 3 H). ^{13}C NMR (60 MHz, CD_3CN): δ = 25.49, 38.28, 50.74, 119.92, 126.95, 130.65, 131.68, 137.49, 153.15, 200.95.

4-Nitrophenylacetophenone (9):[9] Table 1, Entry 3. ^{1}H NMR (250 MHz, CD_3CN): δ = 8.33 (dt, J = 9.10 Hz, J = 1.95 Hz, 2 H), 8.22 (tt, J = 4.25 Hz, J = 1.30 Hz, 1 H), 8.16 (dt, J = 9.10 Hz, J = 1.95 Hz, 2 H), 7.89 (dt, J = 8.52 Hz, J = 1.30 Hz, 2 H), 7.19 (dt, J = 8.52 Hz, J = 1.30 Hz, 2 H), 3.59 (s, 2 H). ^{13}C NMR (60 MHz, CD_3CN): δ = 42.30, 119.34, 127.18, 128.02, 128.91, 130.30, 133.58, 134.96, 137.55, 143.90, 144.20, 197.30.

2,4-Dinitrophenylacetone (10):[5] Table 1, Entry 4. ^{1}H NMR (250 MHz, CD_3CN): δ = 8.98 (d, J = 2.50 Hz, 1 H), 8.45 (dd, J = 8.45 Hz, J = 2.50 Hz, 1 H), 7.65 (d, J = 8.45 Hz, 1 H), 4.41 (s, 2 H), 2.29 (s, 3 H). ^{13}C NMR (60 MHz, CD_3CN): δ = 29.88, 48.44, 120.81, 128.16, 136.05, 138.49, 148.10, 150.07, 202.86.

3-(2,4-Dinitrophenyl)-2-butanone (11):[7] Table 1, Entry 5. ^{1}H NMR (250 MHz, CD_3CN): δ = 8.72 (d, J = 2.50 Hz, 1 H), 8.48 (dd, J = 8.67 Hz, J = 2.50 Hz, 1 H), 7.75 (d, J = 8.67 Hz, 1 H), 4.47 (q, J = 7.18 Hz, 1 H), 2.24 (s, 3 H), 1.55 (d, J = 7.18 Hz, 3 H). ^{13}C NMR (60 MHz, CD_3CN): δ = 25.49, 34.28, 50.76, 119.92, 126.95, 130.65, 131.65, 137.49, 141.80, 205.45.

2,4-Dinitrophenylacetophenone (12):[5] Table 1, Entry 6. ^{1}H NMR (250 MHz, CD_3CN): δ = 8.85 (d, J = 2.35 Hz, 1 H), 8.58 (dd, J = 8.53 Hz, J = 2.35 Hz, 1 H), 7.75 (d, J = 8.53 Hz, 1 H), 7.38 (m, 5 H), 4.92 (s, 2 H). ^{13}C NMR (60 MHz, CD_3CN): δ = 43.39, 119.34, 127.18, 128.02, 128.91, 130.30, 133.58, 134.96, 137.55, 140.20, 143.90, 197.3.

2,4,6-Trinitrophenylacetone (13):[14] Table 1, Entry 7. ^{1}H NMR (250 MHz, CD_3CN): δ = 8.95 (s, 2 H), 4.49 (s, 2 H), 2.23 (s, 3 H).

1-(2,4,6-Trinitrophenyl)-2-butanone (14):[15] Table 1, Entry 8. ^{1}H NMR (250 MHz, CD_3CN): δ = 8.91 (s, 2 H), 3.60 (s, 2 H), 2.33 (q, J = 7.20 Hz, 2 H), 1.00 (t, J = 7.20 Hz, 3 H).

2,4-Dinitronaphthylacetone (15):[16] Table 1, Entry 9. ^{1}H NMR (250 MHz, CD_3CN): δ = 8.61 (s, 1 H), 8.10 (d, *J* = 3.84 Hz, 1 H), 8.04 (m, 1 H), 7.79 (d, *J* = 7.37 Hz, 1 H), 7.71 (m, 1 H), 4.04 (s, 2 H), 2.12 (s, 3 H).

3-(2-Chloro-3-nitro-4-pyridyl)-2-butanone (16): Table 1, Entry 10. ^{1}H NMR (250 MHz, CD_3CN): δ = 8.54 (d, *J* = 4.85 Hz, 1 H), 7.41 (d, *J* = 4.85 Hz, 1 H), 3.90 (q, *J* = 6.85 Hz, 1 H), 2.19 (s, 3 H), 1.45 (d, *J* = 6.85 Hz, 3 H). ^{13}C NMR (62.5 MHz, CD_3CN): δ = 204.77, 150.95, 144.68, 141.12, 123.64, 47.76, 27.98, 16.20. $C_9H_9ClN_2O_3$: calcd. C 47.28, H 3.97, N 12.25; found C 46.99, H 4.18, N 12.07.

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