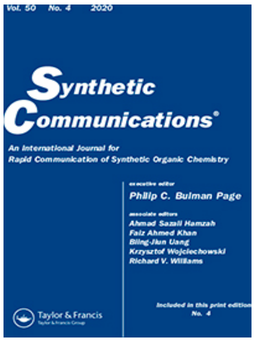

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Iron powder and tin/tin chloride as new reducing agents of Meerwein arylation reaction with unexpected recycling to anilines

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ABSTRACT

Simple and rapid route for Meerwein arylation reaction using iron powder or a mixture of tin/tin chloride has been developed. In the presence of iron powder, different aryl diazonium salts reacted with methyl vinyl ketone, acrylates, and isopropenyl acetate. Production of oximes was detected as the main product with acrylates or in a mixture with β-aryl methyl ketones in the case of methyl vinyl ketone. The *in situ* produced HNO_2 from an excess of $NaNO_2$/HCl was trapped by alkyl aryl radical to form oximes in the *E* configuration form. The presence of tin/tin chloride mixture in the reaction of the aryl diazonium salts with methyl vinyl ketone produced Michael products along with β-aryl methyl ketones. The predicted α-aryl methyl ketones from the reaction of isopropenyl acetate with the diazotized anilines were obtained using iron or tin/tin chloride mixture.

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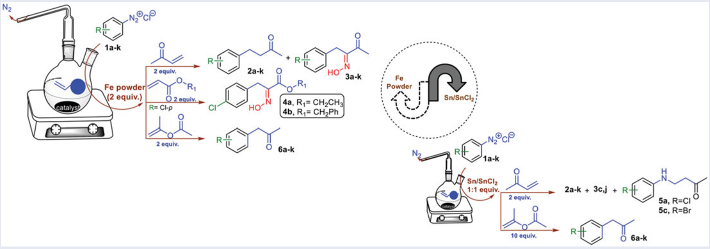
KEYWORDS
Diazonium salt; iron powder; Meerwein arylation; radical reaction; reducing agent; tin; tin chloride

GRAPHICAL ABSTRACT



Introduction

The C–C bond formation is a critical step of great importance in organic synthesis. As an alternative to expensive coupling chemistry, the Meerwein arylation reaction is a highly efficient methodology for this synthesis. Meerwein arylation reaction was

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reported firstly in 1939.[1] It is a simple pathway of furnishing the C-C bond by a reaction between aryl radical and an alkene. The aryl radical is developed by the reduction of diazonium salt using mostly transitional metal salts.[2,3]

Copper salts are the classical and the most employed reducing agent for Meerwein arylation.[4–12] Recently, in 2019, copper(I) was used in its nano form to catalyze Meerwein arylation.[13] Additionally, titanium (III) chloride was used for varieties of activated olefins.[14–16] Besides, silver salt in combination with fluoride sources catalyzed the transformation of styrenes to fluorinated compounds.[17] One of the commonly used metal salts is Fe^{2+} in the form of sulfate for the reaction between functionalized or non-functionalized olefins and the arenediazonium salts.[18–21] $FeSO_4$ was described also to be used in a combination with $TiCl_3$ for synthesizing 1,4-diarylpyrazole derivatives.[22] Additionally, in 2012, iron complex ferrocene (Cp_2Fe) was the solvent-soluble mediator to perform the arylation of ethyl vinyl ether to arylated acetaldehyde by continuous flow synthesis technique.[23]

As an effort to exclude the use of transitional metals, metal-free Meerwein arylation was performed using basic catalysis with activated[24] and non-activated olefins.[25] Also, peroxides,[26] iodide,[27,28] and phenanthroline[28] are considered examples of catalysts replacing the transitional metals[28]. On the other hand, radical photocatalyzed Meerwein arylation in the presence of metal complexes has been developed rapidly in the last years.[29–32]

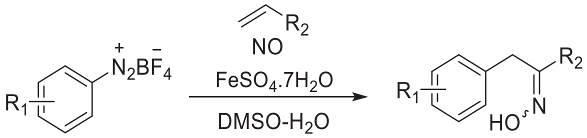
Among all, the reducing agents used for Meerwein arylation and were mentioned previously, the Fe powder or the tin in its elemental or oxidized form has not been recorded before. The importance of Meerwein arylation motivated us to check the reactivity of the Fe powder as well as the tin/tin chloride mixture as reducing agents for expanding the panel of Meerwein's catalysts.

Results and discussion

Following the purpose of present work, the iron powder was investigated as a reducing agent for the reaction of substituted phenyl diazonium salts with activated olefins, namely methyl vinyl ketone and acrylates. We considered the Fe powder as an ideal reducing agent since it is abundant, inexpensive, nontoxic and easily discarded metal.

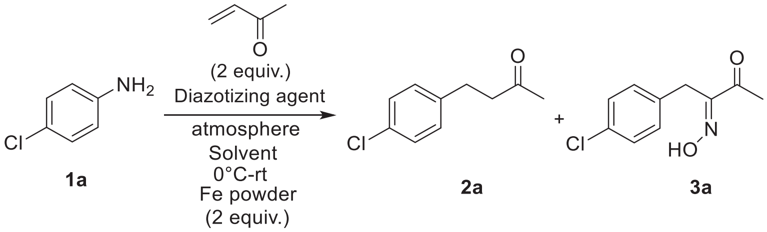
Thus, we began our study with the reaction of *p*-chlorophenyl diazonium salt **1a**, that prepared *in situ* by HCl and $NaNO_2$ with two equivalent of methyl vinyl ketone in acetone-H_2O as a solvent and in the presence of iron powder (2 equiv.). The reaction mixture was extracted with ethyl acetate and purified using column chromatography. The purified fractions showed the β-aryl methyl ketone **2a** which is usually obtained under Meerwein arylation condition[2,14,16] in 40% yield along with a solidified one **3a** in 19% yield. The separated solid was purified by the crystallization process and then became a challenge to be identified.

Compound **3a** was crystallized from cyclohexane as colorless crystals and was assigned the molecular formula $C_{10}H_{10}ClNO_2$ as a result of its molecular ion $[M+Na]^+$ peak at 234.0319 in the HRESI-MS. Its ^1H NMR spectrum (400 MHz, DMSO) revealed two singlet signals at δ_H 3.67 and 2.25 which attributed to the presence of (3H, CH_3) and (2H, CH_2), respectively with no conjugation with each other, besides, a singlet signal at δ_H 12.52 that attributed to the presence of OH. The ^{13}C



Scheme 1. Formation of oximes by NO gas efflux for recycling NO wastes.

Table 1. Optimizing reaction conditions mediated by iron powder.



Entry	Diazotizing agent	Atmosphere	Solvent	Yield (%) 2a	Yield (%) 3a
1	$NaNO_2$/HCl	N_2	DMF–H_2O	0	0
2	$NaNO_2$/HCl	N_2	H_2O	0	0
3	$NaNO_2$/HCl	N_2	DMF/AcOH–H_2O	38	13
4	$NaNO_2$/HCl	N_2	Acetone–H_2O	41	11
5	$NaNO_2$/HCl	Open-air	Acetone–H_2O	40	19
6	$NaNO_2$/HCl/HBF_4	Open-air	Acetone–H_2O	0	0
7	*t*BuONO	Open-air	Acetone–H_2O	0	0

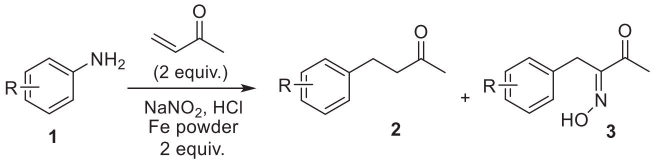
NMR (100 MHz, $CDCl_3$) spectrum showed one resonance corresponding to one carbonyl group (δC 196.3), along with one resonance at (δ_C 158.1) which confirm the presence of (C=N) group. Besides the rest of the aromatic carbons (δ_C 134.6, 132.3, 130.6 (2 carbons), 128.5 (2 carbons)), as well as the methylene (δ_C 27.6) and the methyl group at (δC 25.3), respectively.

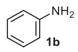
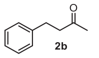
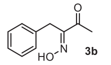
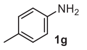
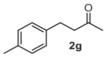
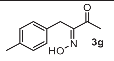
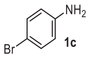
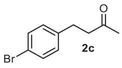
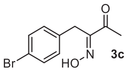
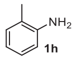
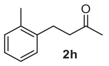
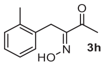
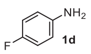
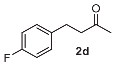
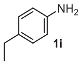
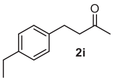
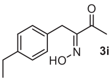
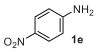
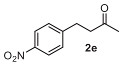
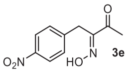
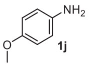
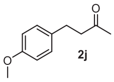
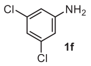
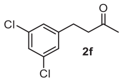
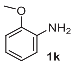
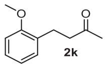
The NMR and mass spectroscopic analysis of compound **3a** suggested a possible similarity to previously prepared oximes by nitric oxide gas efflux through a proposed technique by C. de Salas for recycling NO wastes.[33,34] They developed a technique for denitrification of the industrial wastes through Meerweein arylation catalyzed by $FeSO_4$ $7H_2O$ or Fe(II)-EDTA complex in DMSO-H_2O as a solvent and metal-free in some cases[33,34] (Scheme 1). In which, the arenediazonium tetrafluoroborates reacted with different alkenes including acrylic acid, acrylates, acrylamide, styrenes, allyl acetate, and vinyl cyanide to produce collections of oximes of *E* and *E*/*Z* mixtures[33,34] (Scheme 1).

Based on the above evidence the structure of compound **3a** was assigned as (*E*)-4-(4-chlorophenyl)-3-(hydroxyimino)butan-2-one (Table 1).

The use of Fe powder in the present work was established after several trials of reaction optimization including different parameters: solvent, atmosphere, and diazonium salt (Table 1). The *p*-chlorophenyl diazonium salt was prepared by $NaNO_2$/HCl and the product was accessible in this case. The *p*-chlorophenyl diazonium salt using *t*-BuONO as well as *p*-chlorophenyl diazonium tetrafluoroborate were prepared with no products in the alkylation step.

Table 2. The reaction of methyl vinyl ketone with arenediazonium salts.



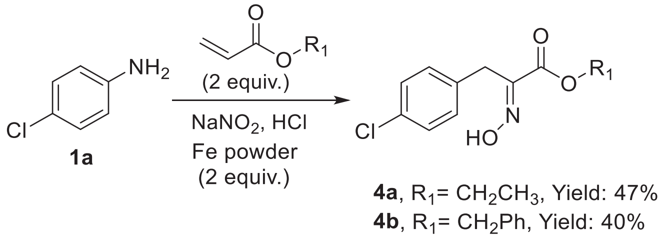
Entry	β-aryl methyl ketones 2	Yield (%)	Oximes 3	Yield (%)	Entry	β-aryl methyl ketones 2	Yield (%)	Oximes 3	Yield (%)
 1b	 2b	24	 3b	19	 1g	 2g		 3g	
 1c	 2c	31	 3c	20	 1h	 2h		 3h	
 1d	 2d	59			 1i	 2i	30	 3i	12
 1e	 2e	7	 3e	25	 1j	 2j	52		
 1f	 2f	30			 1k	 2k	49		

Regarding the atmosphere, the inert gas was initially applied following the typical Meerwein arylation technique,[2,14,16] and we found that the yield was not affected when we switched to open air. On the other hand, the reaction was notably sensitive to the solvent change. Acetone-H_2O mixture seemed to be the most suitable solvent. Whereas, DMF-H_2O did not afford a good vehicle for performing the reaction and no product was collected. Acetic acid offered suitable media even though the drawback of being solidified at 0 °C which was encountered by using AcOH-DMF. Finally, acetone has the advantage of being an easy-evaporation solvent, and thus the acetone-H_2O mixture was designated as a solvent of choice.

After having optimized the reaction conditions we screened different anilines **1b–1k** to react with methyl vinyl ketone (Table 2). The results were identical to those obtained for compound **3a**.

During the progress of our practical work, we tried the reaction of ethyl and benzyl acrylates with the *p*-chlorophenyl diazonium salt employing the previous conditions of preparing **2a–2k** (Scheme 2). The reaction gave the suggested oximes as pure and basic products without any traces of the classical products of Meerwein arylation.

The structures of **4a** and **4b** were clarified based on their elemental analyses and spectral data. The obtained results indicated the formation of oximes. For further confirmation of the structure as well as identification of the type of oxime isomer, a crystal of **4b** was prepared and submitted to X-ray (Figure 1, CCDC 1864773). The oxime was recognized as the *E* isomer, which matched with the proposed results for **3a–3i**.



Scheme 2. The reaction of *p*-chlorophenyl diazonium salt with ethyl acrylate and benzyl acrylate.

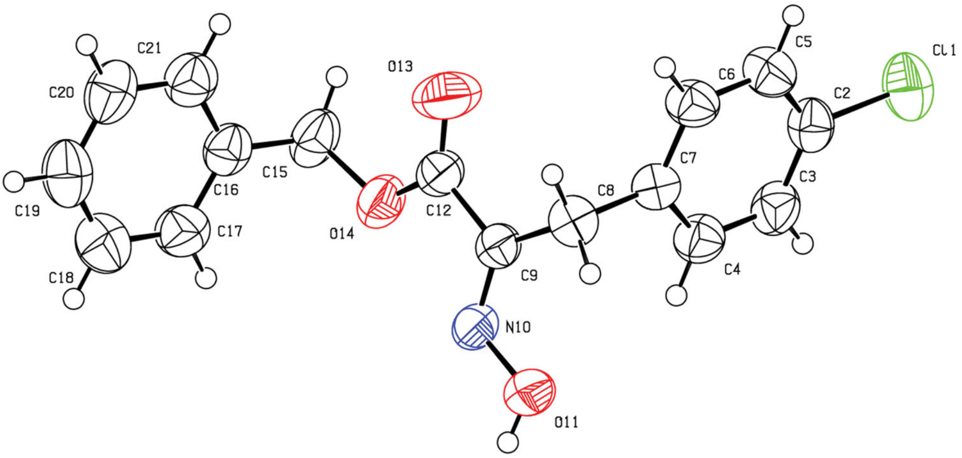
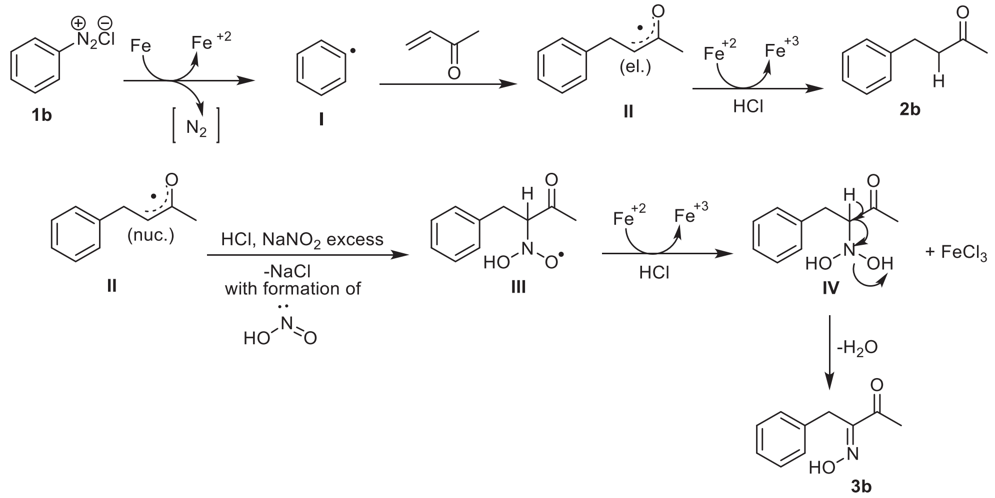


Figure 1. ORTEP structure of **4b**. CCDC 1864773 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Our procedure presented a pathway to prepare the oximes by the excessive $NaNO_2$/HCl rather than nitric oxide gas in C. de Salas condition.[33,34] It is noteworthy to mention that, the compound **4a** was obtained as colorless crystal (m.p. 97–9 °C) in contrast to the physical state which reported for it as brown oil.[33]

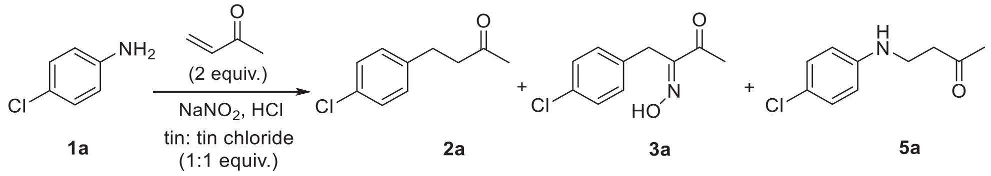
The suggested mechanism for the formation of β-aryl ketones *via* the use of iron powder is depicted in Scheme 3. The radical **I** is generated by oxidation of Fe to Fe^{+2}. The double bond on the functionalized olefin contributes to forming a C-C bond. Then the intermediate **II** is stabilized by the second oxidation of Fe^{+2} to Fe^{+3}. Finally, the acidic media supplies a proton in α-position of the linear chain of phenylbutanone derivatives to yield the classical Meerwein arylation product **2b**.

Regarding the formation of oximes, the pathway is supposedly proceeded by trapping of the intermediate (**II**) by the nitrite (HNO_2); generated from the excess of $NaNO_2$/HCl to give (**III**), which is consequently stabilized by further oxidation of Fe^{+2} to Fe^{+3} and withdraws a proton from HCl in the media to release $FeCl_3$. The final step is accomplished by loss of water to provide the oxime **3b**. It was interesting to observe the color gradient of the reaction medium from the light green to the dark green, which confirms the oxidation of the Fe powder during radicals formation to ferrous chloride; Fe^{+2} and then ferric chloride; Fe^{+3}.



Scheme 3. Proposed mechanism for the formation of β-aryl methyl ketones and oxime via the reaction between the diazonium salt and methyl vinyl ketone using iron metal.

Table 3. Optimizing reaction conditions mediated by tin/tin chloride mixture.



				Yield (%)		
Entry	Diazotizing agent	Reducing agent	Solvent	2a	3a	5a
1	$NaNO_2$/HCl	Tin	DMF–AcOH–H_2O	0	0	0
2	$NaNO_2$/HCl	Tin chloride	DMF–AcOH–H_2O	0	0	0
3	$NaNO_2$/HCl	Tin/Tin chloride	DMF–AcOH–H_2O	40	0	27
4	$NaNO_2$/HCl	Tin/Tin chloride	Acetone–H_2O	0	0	0
5	$NaNO_2$/HCl	Tin/Tin chloride	AcOH–H_2O	Traces	0	0
6	$NaNO_2$/HCl	Tin/Tin chloride	Acetone–AcOH–H_2O	Traces	0	0
7	$NaNO_2$/HCl/HBF_4	Tin/Tin chloride	DMF–AcOH	0	0	0

To test another possibility in this study, tin/tin chloride mixture was investigated as a reducing agent for the reaction of the corresponding aryl diazonium salts of **1a–1k** with methyl vinyl ketone. It's known that tin-metal and tin chloride is operative reducing agents under acidic conditions.[35] The reaction was performed according to the typical method previously reported for iron powder using a stoichiometric amount of tin: tin chloride. Many combinations of tin/tin chloride and solvents were examined to optimize the reaction in order to obtain the desired Meerwien product **3a**. It was found that the exclusive usage of tin or tin chloride didn't help in giving results. Moreover, the addition of AcOH was found very crucial to accomplish the reaction. Switching solvents between DMF and acetone were found to affect the yields and the outputs of the reaction in the favor of DMF as overall results (Table 3).

Table 4. The percentage of recovered anilines.

Anilines	% of recovery
1a	43
1b	46
1c	22
1d	64
1e	Traces
1g	0
1h	0

In the case of *p*-chlorophenyl and *p*-bromophenyl diazonium salts, the classical Meerwien arylation products **2a** (20%) and **2c** (9%) were identified along with the production of amines **5a** and **5c** in 27% and 20% yields, respectively. In contrast to the rest of anilines, the classical Meerwien arylation products were obtained as main products with **1b**, **1g**, **1h**, **1j**, and **1k** in 17–37% yields, whereas, the oximes **3c** and **3g** in 21% and 12% yields were detected along with **2c** and **2g**, experimental part.

The structures of **5a** and **5c** were confirmed based on their elemental analysis and spectral data. The ^{1}H NMR spectral data of **5a** and **5c** were in total agreement with the previous work to be Michael products.[36]

The unexpected results of **5a** and **5c** have been proposed as a result of the return of corresponding anilines **1a** and **1c**. Hereafter the anilines **1a** and **1c** reacted with the unsaturated olefin to produce the corresponding Michael products **5a** and **5c**.

The total output of the reaction of methyl vinyl ketone with aryl diazonium salts that mediated by tin/tin chloride mixture was very low. Augmenting the number of equivalents of methyl vinyl ketone didn't help in the yield enhancement.

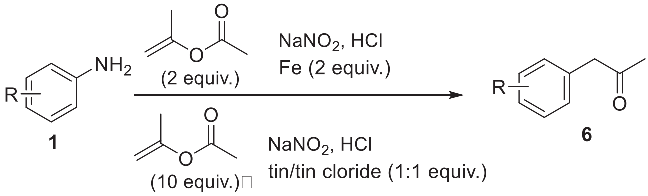
The anilines restoring impacted by the presence of tin/tin chloride mixture was tested for all the aryl diazonium salts under study *via* excluding the olefin from the reaction media to verify the capability of recovering the corresponding anilines after being completely transformed to diazonium salts.

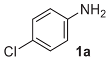
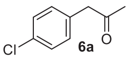
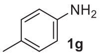
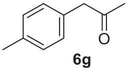
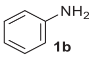
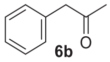
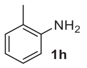
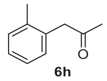
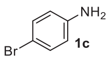
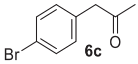
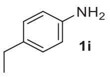
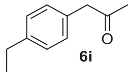
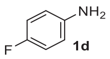
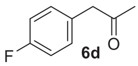
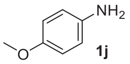
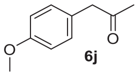
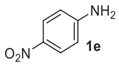
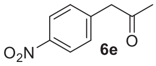
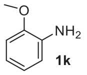
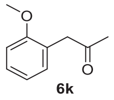
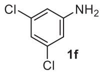
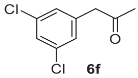
Thus, diazonium salts were prepared by the well-known procedure and precipitated by HBF_4.[37] The solution was tested by TLC to assure the absence of the original anilines. All conditions of Michael adduct production were reestablished without adding the olefin. Iron powder, as well as tin/tin chloride, was deployed to recover the anilines. It was noticed that tin/tin chloride mixture is the reagent that has the capability to transform the radical back to the corresponding anilines. Additionally, the results showed that not all the tested aryl diazonium salts could be restored to their original form (Table 4). The recovering of anilines from their diazonium salts was fairly reported in the literature under a basic condition.[38]

To widen the scope of our research, we used isopropenyl acetate which was employed by C. Molinaro and his coworker to synthesize α-aryl methyl ketones.[24] We applied the previous conditions of the iron powder as well as the tin/tin chloride mixture to investigate their influence on the final products. The reaction behavior was found to follow the same manner of C. Molinaro and produced the expected α-aryl methyl ketones (Table 5).

In the case where the tin/tin chloride mixture is used, we elevated the amount of isopropenyl acetate to 10 equivalents, to help raise the reported product from low to moderate (Table 5). Increasing the number of equivalents of isopropenyl acetate didn't help in the yield enhancement with the Fe powder.

Table 5. The reaction of isopropenyl acetate with aryl diazonium salts.



Entry	α-aryl methyl ketones	Yield %		Entry	α-aryl methyl ketones	Yield %	
		Fe powder	Sn/SnCl$_2$ mixture			Fe powder	Sn/SnCl$_2$ mixture
 1a	 6a	36	51	 1g	 6g	26	44
 1b	 6b	29	69	 1h	 6h	18	55
 1c	 6c	36	47	 1i	 6i	35	45
 1d	 6d	29	0	 1j	 6j	37	27
 1e	 6e	28	54	 1k	 6k	19	42
 1f	 6f	38	56				

Conclusion

We reported here new reducing agents of Meerwein arylation reaction using the iron powder or the tin/tin chloride mixture for the first time. Although iron element was used widely as Fe(II) in the salt of sulfate, it has never been used as iron powder. It was observed that the reaction of aryl diazonium salts with vinyl methyl ketone produced a mixture of *β*-aryl ketones and *E* isomer of oximes in most cases. While the reaction with ethyl and benzyl acrylates led to the formation of the oxime in *E* configuration form as main products. Moreover, the presence of the tin/tin chloride mixture in such reaction of the diazotized anilines with methyl vinyl ketone produced Michael products in a mixture with *β*-aryl methyl ketones. On the other side, the reaction of aryl diazonium salts with isopropenyl acetate led to the formation of the corresponding *α*-aryl methyl ketones under the action of the iron powder or the tin/tin chloride mixture. In summary, despite the advancements of the reported Meerwein arylation methods. The development route of this reaction using the iron powder or the tin/tin chloride mixture seems to be simple, cheap, rapid process, and could be run feasibly on the open air without the need for inert gas.

Experimental

General information

All solvents and reagents were purchased from commercial sources. Melting points were determined with a Büchi 530 digital melting point apparatus and are uncorrected. Elemental analyses were performed on CHNS-O analyzer (Perkin-Elmer, USA) and were found within ±0.4% of the theoretical values.^{1}H and ^{13}C NMR spectra were measured with a Bruker Avance spectrometer (Bruker, Germany) at 400 and 100 MHz, respectively, using TMS as the internal standard. Hydrogen coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Chemical shifts were defined as parts per million (ppm) relative to the solvent peak. High-resolution mass spectra were measured with a MICROTOF-Q ESI/QqTOF (Bruker Daltonics, Germany). Column chromatography was performed using silica gel (60 M, 0.04–0.063 mm) with a proper eluent system. Thin-layer chromatography (TLC) was performed using silica gel plates (POLYGRAM SILG/UV254, 0.20 mm), which were visualized under UV light (254 nm) and by spraying using (vanillin/H_2SO_4/ethanol) mixture. The ketone spot was stained by green color while the oximes were showed as pale yellow after spraying. All reagents and solvents were of commercial grade. Iron metal powder, tin granular and tin chloride (Sigma-Aldrich Chemie GmbH, Export Department Eschenstr.5 82024 Taufkirchen, Germany)

Procedures

General procedure for the preparation of 2a–k, 3a–i, 4a,b, and 6a–k using iron element

To a suspension of aniline **1a–k** (7.8 mmol) in HCl (10 ml, 6 N), a solution of $NaNO_2$ (1.4 g, 20.3 mmol) in water (5 ml) was added slowly over 30 min at 0 °C. Meanwhile, in a two-necked round flask, fitted with condenser and gas bubbler, olefin (15.6 mmol) was dissolved in acetone (20 ml). The diazonium salt solution was added slowly to the stirred olefin solution through a septum by syringe. After complete addition, the iron powder (0.88 g, 15.6 mmol) was added to the reaction mixture 2–3 times. The reaction mixture was stirred at 0 °C until the N_2 evolving ceased, then the reaction mixture was removed from the ice and the stirring was continued at r.t. for another 30 min to 1 h. After the reaction accomplished, the reaction mixture was quenched by water and ice and extracted by ethyl acetate. The products were obtained in pure form after purification by silica gel column chromatography using different eluent systems. The oximes were recrystallized from a proper solvent.

Characterization of compounds 2a–2k

4-Phenylbutan-2-one (2b)[39]

Purified by column chromatography using (DCM–MeOH, 99:1) as yellow oil; yield: iron: 24%, 0.27 g, tin: 26%, 0.15 g; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.33–7.27$ (m, 2H), 7.26–7.17 (m, 3H), 2.92 (t, $J = 8$ Hz, 2H), 2.79 (t, $J = 8$ Hz, 2H), 2.16 (s, 3H).

Characterization of compounds 3a–3i

(E)-3-(Hydroxyimino)-4-phenylbutan-2-one (3b)

Purified by column chromatography using (DCM–MeOH, 99:1) R_f = 0.33 and the obtained solid recrystallized from (MeOH–H_2O, 1:1) as yellow crystals; m.p. 82–4 °C; yield: 17%, 0.23 g; ^{1}H NMR (400 MHz, DMSO) $\delta = 12.45$ (s, 1H), 7.20–7.13 (m, 2H), 7.09 (t, $J = 6.5$ Hz, 3H), 3.68 (s, 2H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 196.7$, 158.5, 136.2, 129.2, 128.4, 126.4, 28.27, 25.40; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{10}H_{11}NO_2Na$: 200.0682; found: 200.0698; Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 68.22; H, 6.15; N, 7.95.

Characterization of compounds 4a and 4b

Ethyl (E)-3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (4a)[33,34]

Purified by column chromatography using (cyclohexane–EtOAc, 4:1) R_f=0.25 as colorless crystals; yield: 47%, 0.89 g; ^{1}H NMR (400 MHz, DMSO) $\delta = 12.53$ (s, 1H), 7.34 (d, $J = 8.6$ Hz, 2H), 7.21 (d, $J = 8.6$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.82 (s, 2H), 1.21 (t, $J = 7.1$ Hz, 3H).

Characterization of compounds 5a and 5c

4-((4-chlorophenyl)amino)butan-2-one (5a)[36]

Purified by column chromatography using (cyclohexane–EtOAc, 4:1) R_f = 0.25 and the obtained solid is white crystals; yield: 27%, 0.2 g; ^{1}H NMR (400 MHz, CDCl3) $\delta = 7.04$ (d, $J = 8$ Hz, 2H), 6.45 (d, $J = 8$ Hz, 2H), 3.94 (s, 1H), 3.31 (t, $J = 6.1$ Hz, 2H), 2.66 (t, $J = 6.0$ Hz, 2H), 2.10 (s, 3H).

The experimental part and spectroscopic data for compounds are available in supplementary files.

Disclosure statement

No potential conflict of interest was reported by the authors.

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