C–C Coupling

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Transition-Metal-Free α-Arylation of Enolizable Aryl Ketones and Mechanistic Evidence for a Radical Process**

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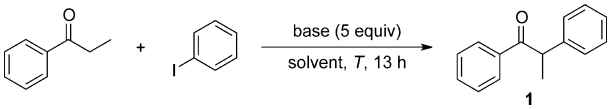
Abstract: *The α-arylation of enolizable aryl ketones can be carried out with aryl halides under transition-metal-free conditions using KO*t*Bu in DMF. The α-aryl ketones thus obtained can be used for step- and cost-economic syntheses of fused heterocycles and Tamoxifen. Mechanistic studies demonstrate the synergetic role of base and solvent for the initiation of the radical process.*

The α-arylation of enolizable carbonyl compounds is a transformation of high importance in synthetic organic chemistry.[1] Semmelhack and co-workers reported the nickel-mediated intramolecular arylation of a lithium enolate as the key step in a total synthesis.[2] The groups of Buchwald, Hartwig, and Miura independently reported methods based on palladium catalysis for the intermolecular α-arylation of ketones.[3] Improved procedures involving palladium or nickel catalysis have since been disclosed.[4] As a complementary approach, our group recently reported the copper-catalyzed α-arylation of benzyl aryl ketones.[5] Whereas transition-metal-catalyzed processes are now commonly employed, methods for the arylation of ketone enolates by radical nucleophilic aromatic substitution ($S_{RN}1$), first reported as early as 1970, are seldom used.[6] These reactions can proceed in the presence of iron or samarium catalysts[7] or without transition metals by photochemical,[8] thermal,[9] or microwave-induced thermal[10] activation. However, these methods have not found widespread use in organic synthesis, probably because of substrate-scope limitations. Indeed, very few procedures describe the $S_{RN}1$ arylation of aryl ketones. The reaction of acetophenone with iodobenzene in DMSO was disclosed, but photostimulation was reported to be mandatory.[8f,g] Other methods make use of pre-formed enolates and activated aryl chlorides in association with metallic potassium or sodium amalgam [Na(Hg)] in liquid ammonia.[8b,9b,d] The specific phenylation of large excesses of preformed aryl enolates or ketones has also been reported using phenylazo *tert*-butyl sulfide[11a] or an excess of a triphenylaluminum isoxazolidine, as the phenyl source, respectively.[11b] Therefore, from a synthetic chemistry point of view, it would be highly desirable to develop general and practical transition-metal-free methods for the arylation of enolizable aryl ketones.

Herein, we describe the potassium *tert*-butoxide promoted α-arylation of various enolizable aryl ketones with aryl halides. We also disclose some evidence to explain the role of KO*t*Bu and DMF in this process and propose a mechanistic pathway based on combined theoretical and experimental studies.

We initially discovered that KO*t*Bu and DMF alone could promote the α-phenylation of propiophenone with iodobenzene with low conversion. Indeed, without a metal catalyst, compound **1** was obtained in low yield (1.2:1 ketone/PhI) using five equivalents of KO*t*Bu in DMF at 40 °C (Table 1, entry 1). Increasing the temperature to 60 °C was moderately beneficial (entry 2), whereas using a 2:1 ketone/PhI ratio at

Table 1: α-Phenylation of propiophenone with iodobenzene.[a]



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Entry	Base	Solvent	Propiophenone/PhI	*T* [°C]	Yield [%][b]
1	KO*t*Bu	DMF	1.2:1	40	37
2	KO*t*Bu	DMF	1.2:1	60	56
3	KO*t*Bu	DMF	2:1	60	99 (97)
4	KO*t*Bu	DMF	2:1	60	85[c]
5	KO*t*Bu	DMF	2:1	23	85[d]
6	LiO*t*Bu	DMF	2:1	60	< 5
7	NaO*t*Bu	DMF	2:1	60	< 5
8	KO*t*Bu	THF	2:1	60	0
9	KO*t*Bu	toluene	2:1	60	0
10	KO*t*Bu	MeCN	2:1	60	0
11	KO*t*Bu	DMSO	2:1	60	< 1

[a] Reactions were performed on a 1 mmol scale in 3 mL of the indicated solvent. [b] Yield determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. Yields of isolated products are given in parentheses. [c] The yield was 85 % when either 5 equivalents of DMF (380 μL) or undistilled DMF (3 mL) under an air atmosphere were used. [d] 48 h; 99 % yield after 72 h.

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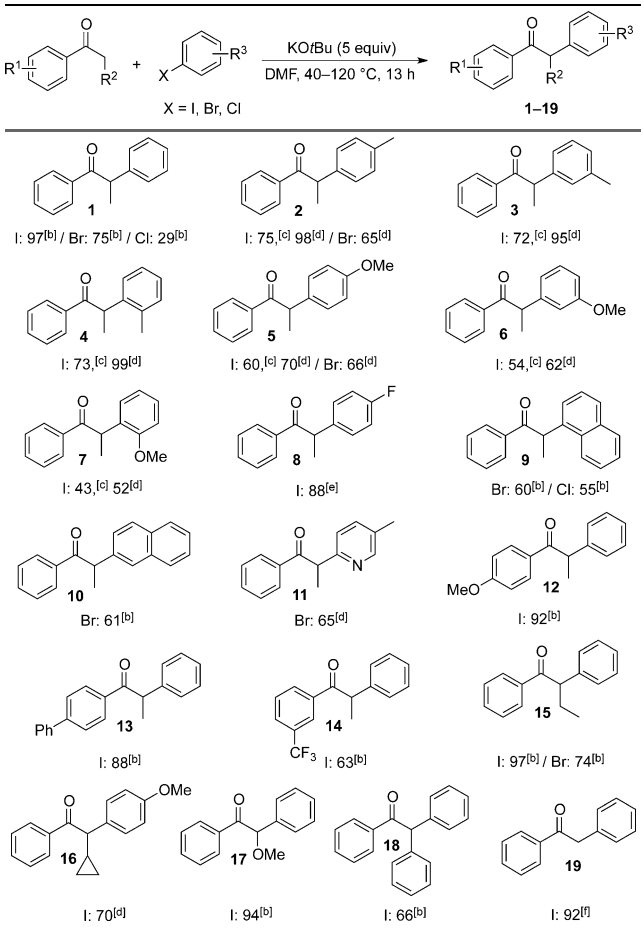
60 °C led to a quantitative yield (entry 3). The reaction also proceeded smoothly when either five equivalents of DMF or undistilled DMF under an air atmosphere were used, as an 85 % yield was obtained in both cases (entry 4). Interestingly, the reaction was also efficient at room temperature, giving 85 % yield after 48 hours (99 % yield after 72 h; entry 5). Among the other bases tested, LiO*t*Bu and NaO*t*Bu gave very poor conversion (entries 6 and 7). A solvent screen revealed that THF, toluene, acetonitrile, and DMSO were unsuitable for this reaction (entries 8–11). Therefore, it is clear that KO*t*Bu/DMF is the combination of choice.[12] Being aware of the fact that undesired metal contaminants in commercial KO*t*Bu could catalyze the reaction,[13] we resublimed the base. Using this purer base led to the same quantitative yield (entry 3).[14]

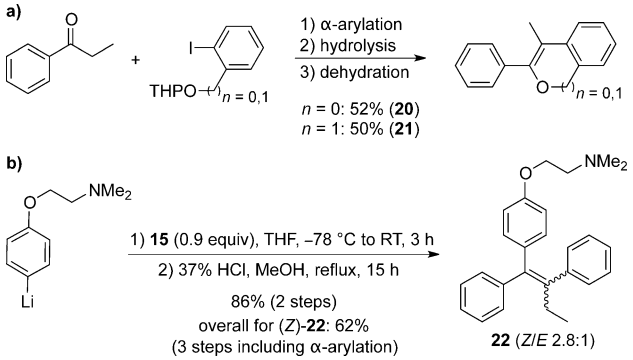
We subsequently turned our attention to the scope of the reaction (Table 2). Under the standard conditions, the three iodotoluene isomers (*ortho*, *meta*, *para*) gave good yields of **2**–**4**. The substitution pattern thus has little impact on the reaction outcome. Using a larger amount of propiophenone (4 equiv) led to quantitative yields of **2**–**4** (the excess ketone was completely recovered following chromatography). Moderate to good yields were obtained for the three iodoanisole isomers (**5**–**7**). For these substrates, using an excess of ketone (4 equiv) slightly increased the yields. Compound **8** was synthesized in very good yield from 1-fluoro-4-iodobenzene. Compounds **12**–**14** were obtained in good to excellent yields from electron-rich or electron-poor propiophenones. The reaction also proceeded efficiently in the presence of electron-donating (Et, cyclopropyl, OMe: **15**–**17**) or electron-withdrawing (Ph: **18**) substituents at the enolizable position, although the reaction was completely shut down when a stronger deactivating group (CN) was employed. Acetophenone is also a suitable substrate for the coupling with iodobenzene, and the corresponding α-arylation product **19** was indeed isolated in excellent yield (92 %); traces of the disubstitution product **18** were also obtained.[15] Importantly, bromoarenes could also be used, giving products **1**, **2**, **5**, and **9**–**11** in moderate to very good yields, but the reactions had to be heated to 120 °C. Interestingly, chloroarenes could be used in two cases. Product **1** was obtained in a low yield of 29 % from chlorobenzene, whereas the use of 1-chloronaphthalene resulted in the isolation of **9** in a promising yield of 55 %.

An interesting application of this method is the synthesis of fused heterocycles (Scheme 1 a).[16] After protection of 2-iodophenol and 2-iodobenzylalcohol as the tetrahydropyranyl (THP) acetals, benzofuran **20** and 1*H*-isochromene **21** were obtained.[17] Tamoxifen (**22**; *Z*/*E* 2.8:1) could also be synthesized in a three-step sequence (Scheme 1b).[18] Overall, active (*Z*)-Tamoxifen (**22**), the most prescribed drug for the treatment of breast cancer worldwide,[19] was obtained in 62 % yield (the *E* isomer can be selectively crystallized),[20] and a scale-up to 20 mmol of PhBr is possible.

Table 2: Scope of the α-arylation of enolizable aryl ketones with aryl halides.[a]



[a] Reactions performed on a 1 mmol scale, yields of isolated products are given. [b] The reaction conditions of Table 1, entry 3, X = I, *T* = 60 °C (for X = Br or Cl, *T* = 120 °C). [c] The reaction conditions of Table 1, entry 3, *T* = 80 °C. [d] *T* = 60 °C, enolizable ketone/aryl halide = 4:1 (for X = Br, *T* = 120 °C). [e] *T* = 40 °C, enolizable ketone/aryl halide = 4:1. [f] *T* = 23 °C, 48 h, X = I, acetophenone/PhI = 2:1.



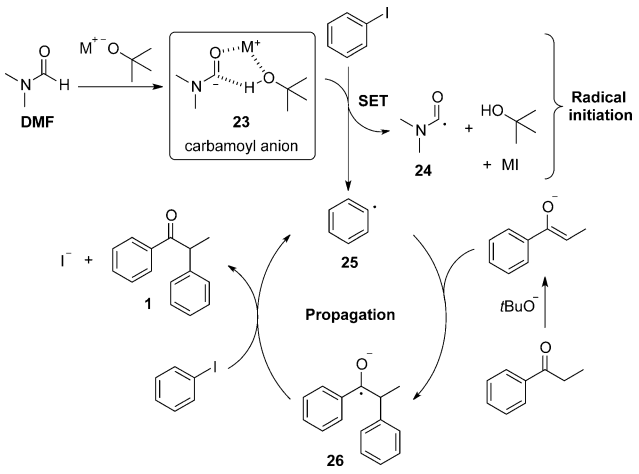
Scheme 1. Syntheses of fused heterocycles and Tamoxifen (see the Supporting Information for details).

As we suspected the reaction to proceed through radical intermediates, we added some common radical scavengers. Galvinoxyl and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) completely inhibited the coupling of propiophenone with iodobenzene. Complementary experiments showed that the reaction was not inhibited in the dark (78 % yield of **1** after 48 h at room temperature), and good conversions were

achieved under UV irradiation (46% yield after 2 h at room temperature, $\lambda = 365$ nm). Previous work on homolytic aromatic substitution (HAS) already evoked the possibility that potassium *tert*-butoxide could be involved in a ligand-assisted[21] direct electron transfer to an aryl halide, such as iodobenzene.[22] However, owing to the extremely unfavorable energy variation computed for this reaction ($\Delta E = 50.51$ kcal mol^{-1} for KO*t*Bu + PhI → Ph$^{\bullet}$ + *t*BuO$^{\bullet}$ + K$^+$ + I$^-$ in DMF, see below for computational details),[23] its role as a radical initiator seemed very unlikely. This is in agreement with the conclusion drawn by Murphy and co-workers,[24] although their proposal of benzyne intermediates is inconsistent with the absence of regioisomers in our reaction (only *ipso* substitution occurred). Moreover, all of these mechanisms are not able to explain the key role played by the solvent and the potassium cation.

The hypothesis[25] of Yan and co-workers, namely that an electron-rich carbamoyl anion is generated by the deprotonation of DMF with KO*t*Bu, seems more reasonable to explain the experimental observations. The formation of this intermediate was first reported by Reeves and co-workers.[26] In our case, ^{1}H and ^{13}C NMR experiments confirmed the rapid exchange of the formamide proton in a solution of KO*t*Bu in wet [D$_7$]DMF (see the Supporting Information). It is noteworthy that no proton exchange was observed after 12 hours under the same conditions when NaO*t*Bu was used instead of KO*t*Bu, which might be due to the lower solubility of the former base. Furthermore, we were not able to detect the dimerization product of DMF even after prolonged reaction times.

On the basis of these experiments, we postulate a radical chain mechanism in which the solvent acts as the initiator of the overall process (Scheme 2). The *tert*-butoxide anion abstracts a proton from DMF, generating carbamoyl anion **23**, which can be stabilized by the interaction with the associated cation M$^+$ and *tert*-butanol. Anion **23** then transfers an electron to the aryl halide, generating X$^-$ and arene radical **25** along with the carbamoyl radical **24**, which is stabilized by interactions with both MX and *t*BuOH (see the Supporting Information). Propagation then follows an S$_{RN}$1 pathway. The arene radical **25** undergoes coupling with an enolate to generate radical anion **26**. A final SET from **26** to another aryl halide molecule releases α-aryl ketone **1**.

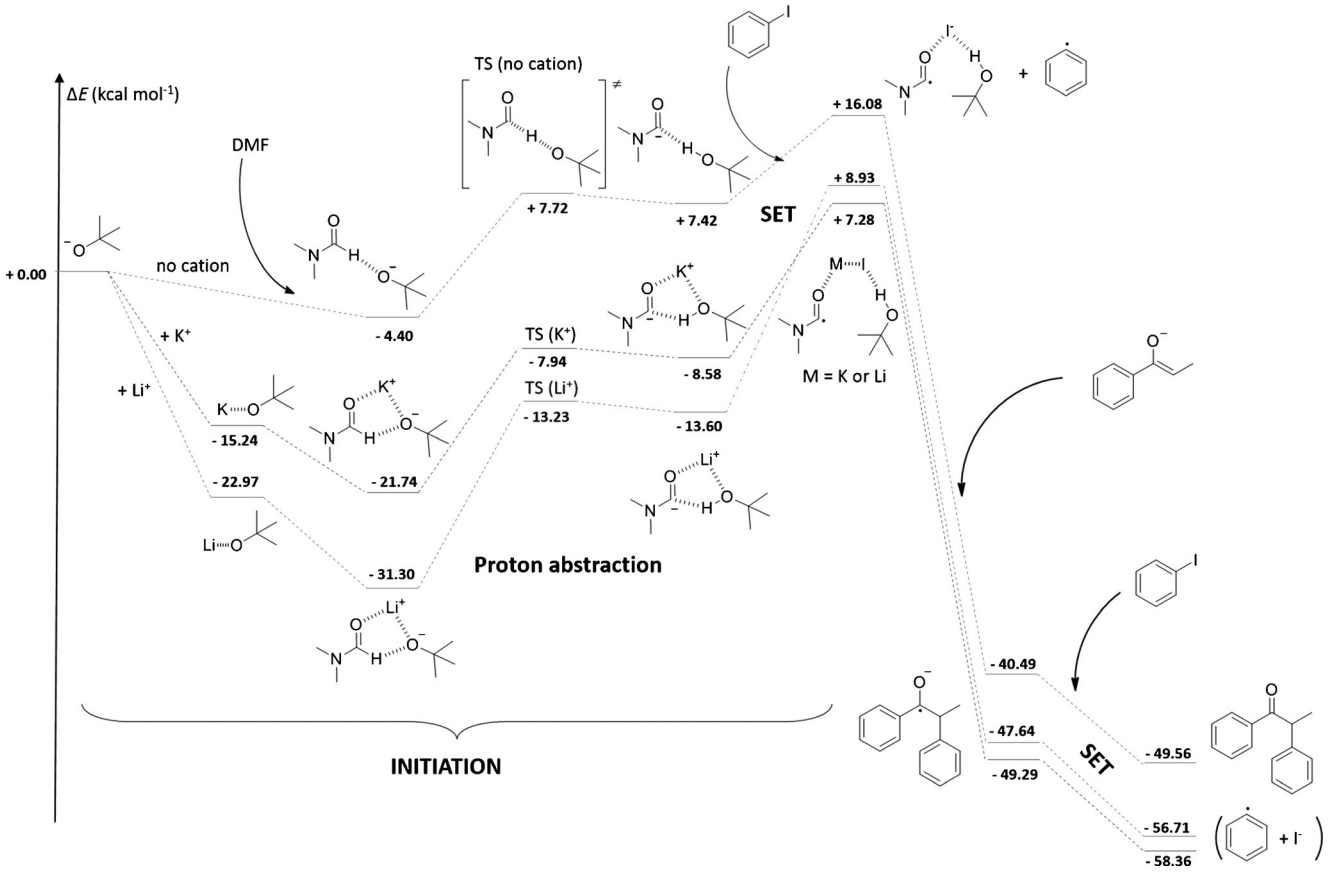


Scheme 2. An S$_{RN}$1 mechanism as the proposed mechanistic pathway.

This hypothesis was confirmed at the theoretical level using density functional theory (DFT) calculations at the M06-2X/6-311 + G(d,p) level of theory; bulk solvent effects were included by means of a polarizable continuum model (PCM; Scheme 3, see the Supporting Information for details).[27] The reaction paths computed in the absence and in the presence of the cation (K$^+$ or Li$^+$) were thus compared. DMF and *t*BuO$^-$ are able to form a stable intermediate owing to hydrogen bonding ($\Delta E = -4.40$ kcal mol^{-1}). However, the presence of a cation leads to much more stable complexes: $\Delta E = -21.74$ kcal mol^{-1} for K$^+$ and $\Delta E = -31.30$ kcal mol^{-1} for Li$^+$. Successive deprotonation is then achievable with a reasonably low activation barrier: $E_a = 12.12$ kcal mol^{-1} (no cation), $E_a = 13.80$ kcal mol^{-1} (K$^+$), and $E_a = 18.07$ kcal mol^{-1} (Li$^+$). In all cases, the computed transition state is very close in energy to the product of the reaction, a carbamoyl anion stabilized by *tert*-butanol through hydrogen bonding. Overall, the computed reaction barriers are consistent with the experimental conditions and clearly show the synergetic role played by the base and the solvent in the initiation process.

The electron-rich carbamoyl anion can thus react with PhI through a SET mechanism to form the corresponding benzene radical **25**. Calculations showed that the radical anion of iodobenzene dissociated spontaneously to the corresponding iodide anion and benzene radical **25**. The variation of the total energy associated with this SET process is computed to be higher in the presence of K$^+$ ($\Delta E = 15.86$ kcal mol^{-1}) and Li$^+$ ($\Delta E = 22.53$ kcal mol^{-1}) than in the absence of a cation ($\Delta E = 8.66$ kcal mol^{-1}), and this dissociation actually represents the rate-determining step of the reaction. From a thermodynamic point of view, the overall reaction is driven by the last steps, which are extremely favorable. Indeed, a ΔE value of -56.57 kcal mol^{-1} was computed for the reaction of the enolate with the benzene radical **25** to form radical anion **26**, which can then react (by SET) with PhI ($\Delta E = -9.07$ kcal mol^{-1}) to yield the final product, along with the regeneration of the benzene radical **25**.

Whereas the roles of DMF and *t*BuO$^-$ are relatively clear from the computed reaction paths, it is more delicate to define the role of the cation and to justify the peculiar efficiency observed with K$^+$. It is clear that the cation can help in the stabilization of reaction intermediates. Indeed, the lower barrier found in the presence of potassium with respect to lithium can give some, albeit non exhaustive, information on the role of the cation. Too much stabilization, such as in the case of Li$^+$, can be deleterious, as it translates into too high reaction barriers (for deprotonation) or energies (SET). It is indeed important to stress that all issues related to solubility, which can play a role in this process, cannot be addressed by this computational method. It is important to note that owing to the difficulty associated with estimating the energy of formation of LiI and KI in solution using the current theoretical approach, the computed energy values associated with the SET elementary step should be considered as an



Scheme 3. Energy profiles computed for the $S_{RN}1$ pathway in DMF at the M06-2X/6-311 + G(d,p) level of theory; ΔE values are given in kcal mol^{-1}.

upper boundary to the reaction energies. As a result, even if the SET energies are overestimated, the overall conclusions of this mechanistic study will not be affected.

Cyclic voltammetry experiments support the fact that the cation promotes the SET process, as the reduction potential of PhI is lowered when alkali salts are added to the reaction mixture; the cation favors the formation of the arene radical **25** from PhI by capturing the iodide anion (see the Supporting Information).[28]

In conclusion, we have disclosed conditions for the transition-metal-free α-arylation of various enolizable aryl ketones with aryl halides.[29] Experimental and computational studies provide unambiguous evidence that DMF is an active species in the initiation step. Under the experimental conditions, deprotonation of this solvent is indeed possible, and the carbamoyl anion thus generated is able to promote the $S_{RN}1$ process, which leads to the formation of α-aryl ketones. Further developments will be reported in due course.

Keywords: arylation · C–C coupling · ketones · reaction mechanisms

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[15] Starting from PhI, the expected product was obtained in very low yield under our standard conditions when dialkyl ketones were employed, whereas with α-tetralone, no reaction was observed.

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