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Advances in amidation chemistry – a short overview

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Dedicated to Prof. Sambasivarao Kotha for his significant contributions in new synthetic methods development using transition metal catalysts.

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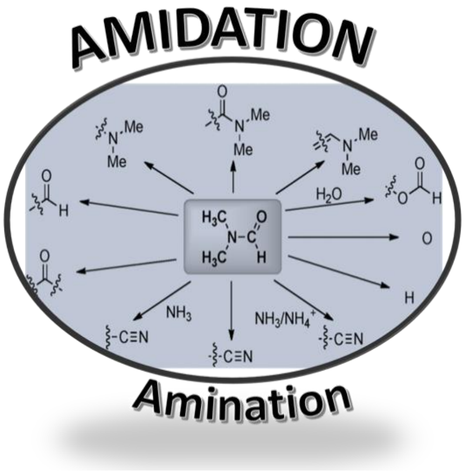
Abstract

In synthetic organic chemistry, N,N-dialkylamides, such as *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA), are utilized as all-purpose reagents. They may be utilized in a variety of ways to construct various functional groupings and are affordable, easily accessible, and adaptable building blocks. Numerous publications in recent years have demonstrated the excellent and practical uses of *N,N*-dialkylamide in the synthesis of heterocycles, formylation (R-CHO), amidoalkylation (-R), cyanation (R-CN), aminocarbonylation (R-CONMe$_2$), formylation (R-CN), methylene group (R-CH$_2$), and amino acids (R-NMe$_2$). This minireview discusses significant advancements in the synthesis of heterocycles and the functionalization of open-chain systems using *N,N*-dialkylamides, especially DMF.



Keywords: *N,N*-Dimethylformamide, amination, amidoalkylation, aminocarbonylation, cyanation, formylation

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1. Introduction

N,N-Dimethylformamide (DMF) is primarily used as a polar solvent in a variety of chemical processes. DMF is also a versatile reagent that is commonly used in chemistry. DMF, for example, can be used as an effective ligand in the production of metallic complexes.[1] In addition to acting as a source of various important intermediates, DMF can react as an electrophile or a nucleophile and can play a role in reactions as a dehydrating agent, a reducing agent, a catalyst,[2–5] or a stabilizer.[6–9] For the synthesis of metallic compounds DMF can be an effective ligand. *N,N*-dialkylamides could be considered as a combination of several functional groups such as alkyl, amide, carbonyl, dialkyl amine, formyl, N-formyl and highly polar C-N, C=O, and C-H bonds. Due to flexible reactivity of *N,N*-dialkylamides, during the past few years, chemists have succeeded in developing reactions, where DMF and DMA could be used to deliver different functional groups such as -CO, -NMe_2,-$CONMe_2$, -Me, -CHO, etc., a single atoms such as C, O, H etc. (Figure 1). Similarly, DMF could be used in the preparation of heterocyclic compound through formylation of active methylene groups, conversion of methyl groups to enamines, and formylation of amino groups to amidines. Further, it can also be utilized as an intermediate in the modification of heterocyclic compounds.[10]

Muzart's[1] seminal review highlighted the role of DMF in organic synthesis until 2009; Ding and Jiao's comprehensive review in 2012 covered DMF as a multipurpose precursor for various reactions.[11] Additionally, Batra et al. [12] conducted a comprehensive review of DMF as a reagent for various applications and reviewed the triple function of DMF as a catalyst, reagent, and stabilizer. [13,14]

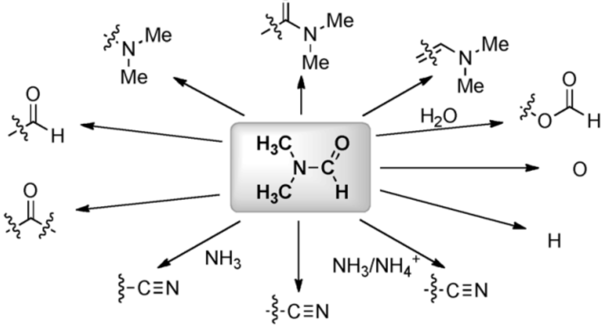


Figure 1. Dimethylformamide as precursor/synthon for various functional groups [11].

In this review we summarize developments on applications of DMF in reactions such as amination (R-NMe_2), formylation (R-CHO),[15,16] as a single carbon source (R-C), methylene group (R-CH_2),[17] carbonylation (R-CO), as well as newer reactions such as amidoalkylation (-$CH_2N(CH_3)$-C(=O) CH_3-R),[18] metal catalyzed aminocarbonylation (R-$CONMe_2$),[19] cyanation (R-CN),[20,21] and, formation of heterocycles, which took place during the past few decades and up to October 2019. Heterocycles are essential compounds used in various applications, from materials to medicines. This unlike other reviews appeared on this subject,[1,22] we provided special emphasis on reactions involving DMF. Although DMF can serve as a reagent in organic reactions such as Friedel- Crafts [23] and Vilsmeier-Haack [24] reactions the actual reagent is derivative of DMF, hence we did not cover such subjects. We hope this review will stimulate further research interest on the application of DMF in organic synthesis.

2. DMF Mediated Aminocarbonylation Reactions

Hiyama et al.[25] (Figure 2) established an effective approach for obtaining benzamides **2** by aminocarbonylation of aryl and alkenyl iodides **1** using DMF as an amide source in the presence of a Pd/$POCl_3$ catalytic system. Similarly, Indolese et al. demonstrated under pressure aminocarbonylation of aryl halides **1** using a Pd catalyst and a triphenylphosphine ligand in a CO environment. DMAP is utilized as the base in this reaction, and the yield is quite high.[26] It is an essential synthetic approach since it may also be used to synthesize pyridine and thiophene halides (Figure 2).

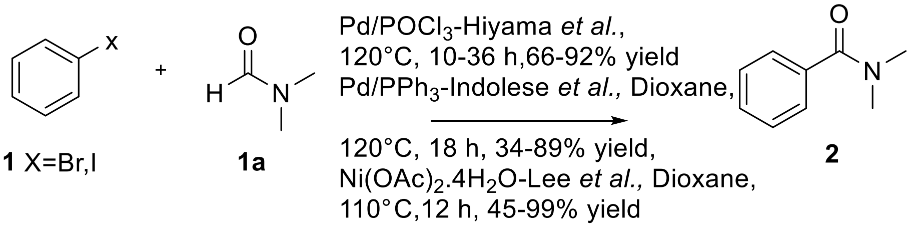


Figure 2. Metal catalyzed aminocarbonylation of aryl halides using DMF.

Furthermore, Lee and colleagues established the same reaction between aryl bromides/iodides **1** and DMF in dioxane solvent using phosphite ligand and sodium methoxide as base (Figure 2).[27] Wang et al. demonstrated a metal-free radical amidation of thiazoles and oxazoles **3** using a series of formamides and *tert*-butyl perbenzoate (TBPB) as radical initiator. High yields of amidated azoles **4** were easily produced using this approach (Figure 3).[28]

Wang et al., demonstrated direct amidation of alcohols **5** with formamides in the presence of an I_2/TBHP with sodium hydroxide as a base and DMF as amide source (Figure 4).[29] The same author reported amidation of benzylamine **5a** under the acidic condition.[30] Feng and co-workers proposed green protocol for the synthesis of α-ketoamides **6** through TBAI catalyzed sp^3 C-H oxidative radical/radical cross-coupling. This method is applicable for broad range of substrates.[31] The only by product is water and no CO or CO_2 emission is observed (Figure 5).

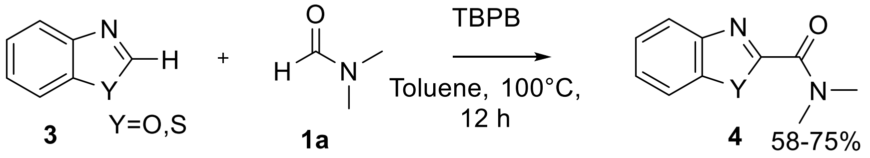


Figure 3. DMF as a source for aminocarbonylation of azoles.

Similarly, α-ketoamides **6a** using aryl methyl ketones **7** were synthesized utilizing widely accessible N,N-dialkylformamides in the presence of nBu_4NI and aq. TBHP as catalyst and oxidant for the radical oxidative coupling process (Figure 5). Mai et al. devised this technique as a green and metal-free solution.[32]

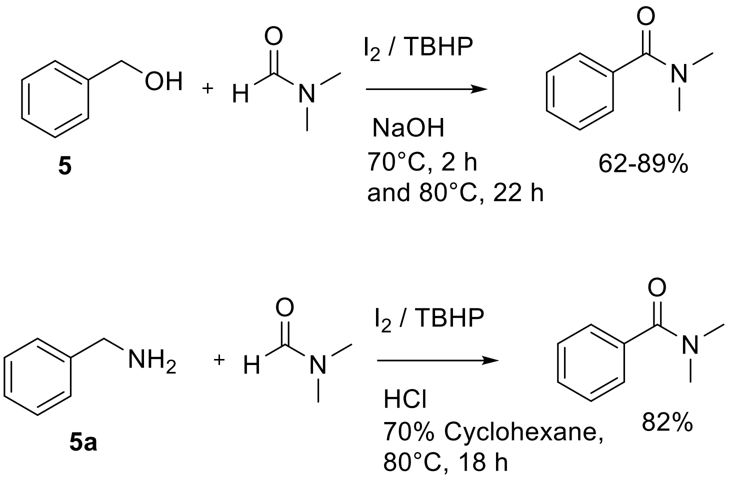


Figure 4. DMF as a source for aminocarbonylation of alcohol and amines.

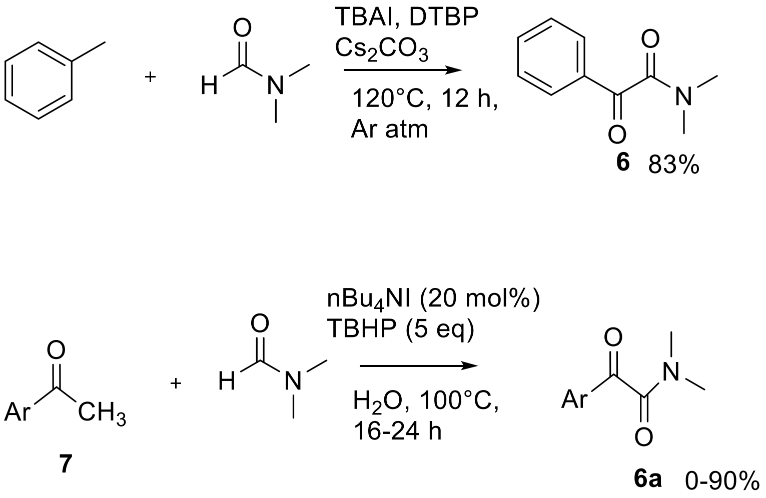


Figure 5. DMF as aminocarbonylation source in synthesis of α-ketoamides.

In 2016, Xiao and his colleagues discovered a simple and effective method for synthesizing amides **2** by cross coupling carboxylic acids **8** with N-substituted formamides in the presence of a Ru catalyst, and the appropriate amide was produced following CO_2 release (Figure 6). The carbonyl group in the amide product was formed by benzoic acid rather than N-substituted formamides. This synthetic approach is stable, low toxicity, and environmentally benign. This approach is effective with several carboxylic acid derivatives and N-substituted formamides.[33]

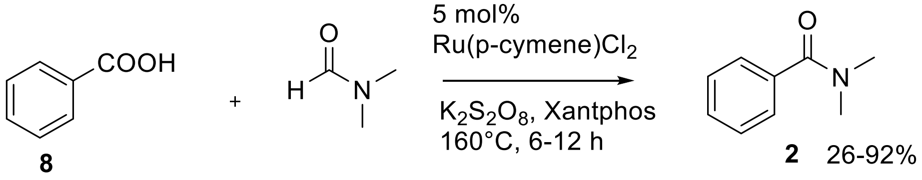


Figure 6. DMF in Ru-catalyzed amidation of carboxylic acids.

Similarly, Tortoioli and colleagues showed metal-free one-pot synthesis of dialkyl amides using benzoic acid and DMF in the presence of propyl phosphonic anhydride (T_3P) and acid additives.[34] This gentle approach was used to create triazinate, a dihydrofolate reductase inhibitor. (Figure 7).

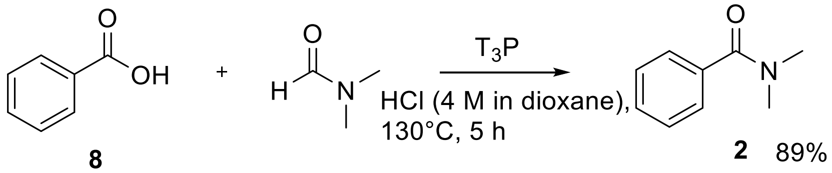


Figure 7. Amidation of benzoic acid with DMF.

Bhat et al. **10** reported direct carbonylation of heterocycles **9** by direct dehydrogenative aminocarbonylation in the absence of transition metals (Figure 8). Persulfate, which served as an effective oxidant, a good radical initiator, a moderate and environmentally favourable low-cost reagent, and formamides served as reagents in the formation of primary to tertiary carboxamides.[35]

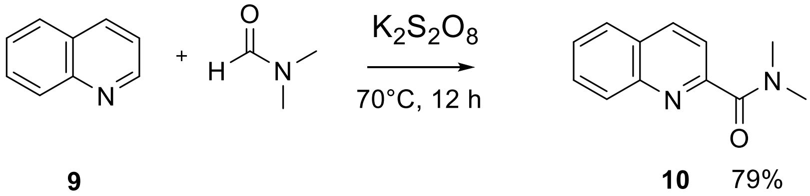


Figure 8. DMF as source for aminocarbonylation of quinoline.

Bhisma et al. demonstrated an efficient copper catalyzed synthesis of phenol carbamates **11** from dialkylformamides as an aminocarbonyl surrogate and phenols with directing groups such as benzothiazoles, quinoline, and formyl at ortho-position (Figure 9). It is a low-cost and environmentally benign reaction that tolerates a wide range of functional groups and provides a phosgene-free path to carbamates.[36]

Phan and colleagues created organic carbamates **13** employing metal organic framework $Cu_2(BPDC)_2(BPY)$ (BPDC = 4,40-biphenyldicarboxylative, BPY = 4,40-bipyridine) as heterogeneous catalyst for cross dehydrogenative coupling of DMF with 2-substituted phenols **12** under oxidative conditions (Figure 10). This catalyst has a higher catalytic activity and is easily recovered and reused.[37]

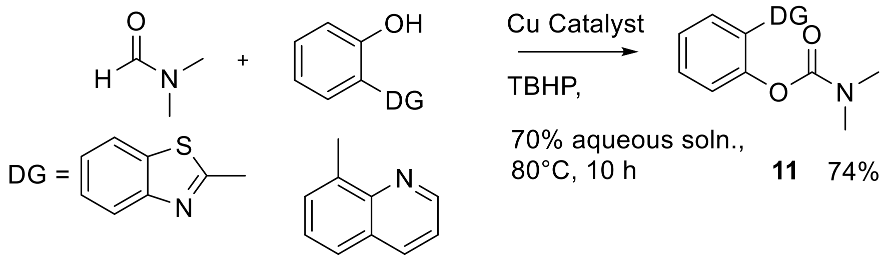


Figure 9. Carbamate synthesis from phenols and formamides.

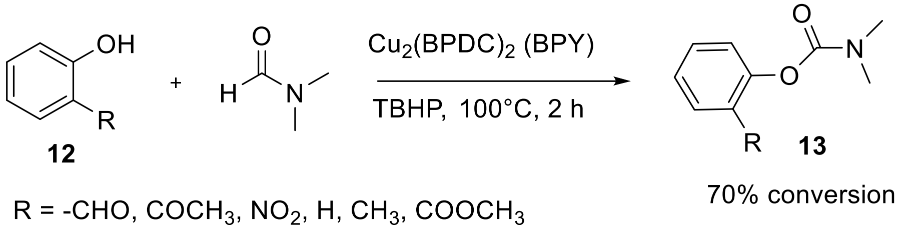


Figure 10. Cross-dehydrogenative coupling reaction of phenol with DMF.

Yuan et al. synthesized *S*-phenyldialkylthiocarbamate **15** compounds under solvent-free conditions using a TBHP-promoted radical pathway in which formamide acyl C-H bonds were directly oxidized in the presence of $Cu(OAc)_2$ to form the reaction intermediate for formamide oxidative coupling with thiols **14** (Figure 11).[38] This procedure is both efficient and environmentally friendly.

Kamal and colleagues devised a more efficient and environmentally friendly technique for synthesising selenocarbamates **17** by an oxidative coupling reaction between formamides and diselenides **16** in metal-free circumstances (Figure 12). A metal-free approach to direct C-Se bond synthesis happened at carbonyl carbon employing TBHP and molecular sieves under simple reaction conditions. This reaction has the benefit of using a non-functionalized substrate.[39]

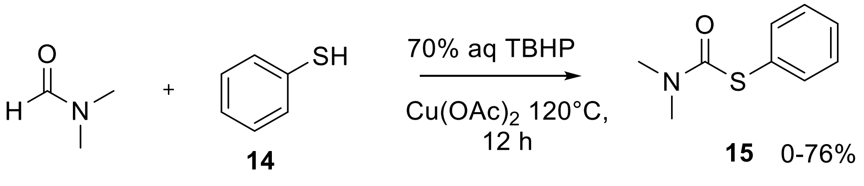


Figure 11. Synthesis of *S*-phenyldialkylthiocarbamate.

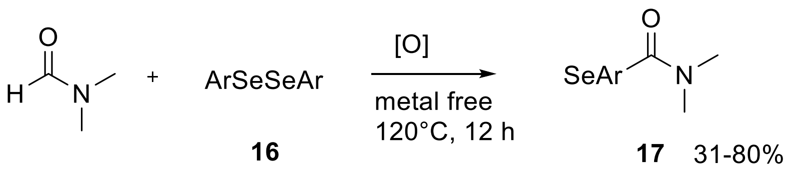
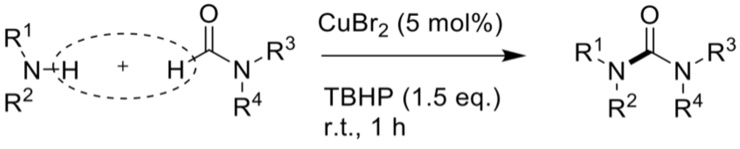


Figure 12. Oxidative C-Se coupling of formamides and diselenides.

Kantam et al. created unsymmetrical urea derivatives **19** by copper catalyzed C-H/N-H coupling of formamides (both mono and di) with various amines **18** (primary, secondary, and modified aromatic amines) and radicals. The significance of this green reaction is that it eliminates the usage of pre-functionalized substrates, which saves atoms.[40] (Figure 13)



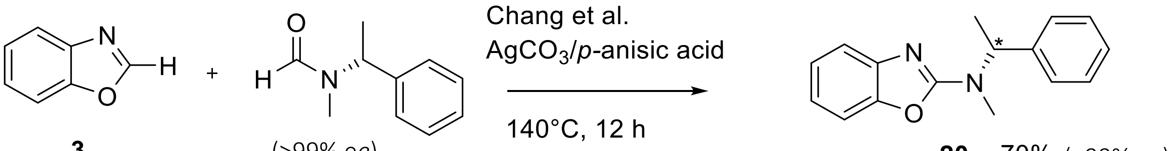
18 **19**

Figure 13. Synthesis unsymmetrical urea derivatives from DMF.

3. DMF Mediated Amination Reactions

The direct amination of C-H bonds has been investigated as a less harmful alternative to the Ullmann-Goldberg and Buchwald-Hartwig aminations, which use (hetero)aryl halides or their equivalents to react with amines. Significant research is being conducted to develop an optimal C-H amination system that combines inactivated hydrocarbons with easily accessible amino sources under moderate circumstances while creating minimum waste.[41,42]

Chang et al. reported that after treating benzoxazoles **3** with optically active formamide, (R)-N-methyl-N-(1-phenylethyl)-formamide (>99% *ee*), in the presence of an acid additive and using Ag_2CO_3 as a catalyst, 2-aminated benzoxazole **20** was produced as a single product in reasonable yield (Figure 14). Surprisingly, this approach is also applicable to optically active formamide, since the target product was produced in higher yield without racemization.[43]



3 **20** 70% (>99% *ee*)

Figure 14. Amination of benzoxazole using Ag_2CO_3 catalyst.

Li et al. developed a method for the synthesis of 2-aminoazole derivatives **20** in which the C-N bond of azoles **3** is formed either by decarboxylative coupling with formamides as a nitrogen source or by direct C-H amination with secondary amines as a nitrogen source using an inexpensive Cu catalyst, O_2 or air as an oxidant, and benzoic acid plays a major role in the release of amine from amides.[44] Yu et al. also discovered a decarbonylative coupling between azoles and formamides. In the presence of formamides and amines as nitrogen sources, iron catalyzed direct C-H amination of azoles at C_2 (Figure 15). Under air, easily available iron (II) salts worked as Lewis's acids, activating the C_2 position of benzoxazoles **3** and acting as an oxidant, while imidazole was utilized as an addition in the catalyst. Direct azole amination was catalyzed by cheap and environmentally friendly reagents. The reaction was also carried out in the presence of acetonitrile with amines.[45]

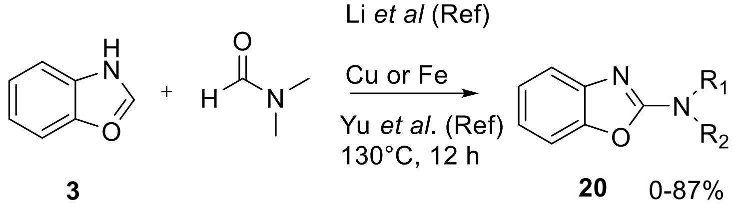


Figure 15. Amination of benzoxazole using Cu or Fe catalyst.

Peng and colleagues devised a simple and effective one-pot synthesis of 2-acyl-4-(dimethylamino)-quinazoline **22** by direct amination of 2-aryl quinazoline-4(3H) ones **21** with DMF, with 4-toluene sulfonyl chloride acting as a C-OH bond activator (Figure 16). As a base, KO*t*-Bu was utilized, which results in the synthesis of tosylate, which attacks DMF, which then undergoes hydrolysis to provide aminated product. This process is cheap and employs simple reagents.[46]

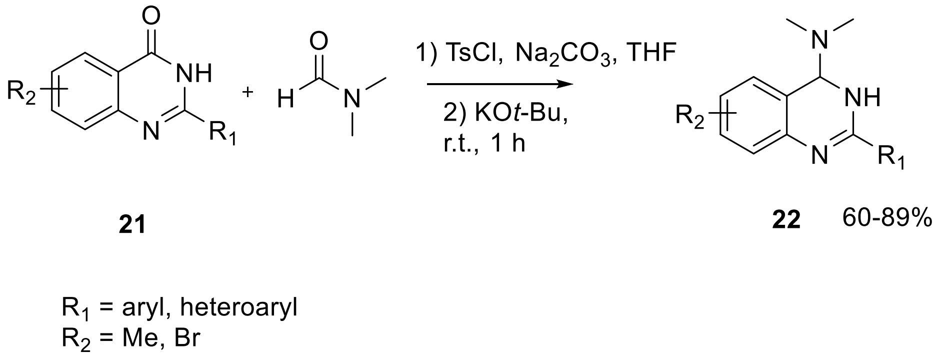


Figure 16. Direct amination of 2-aryl quinazoline-4(3*H*)ones with DMF.

Eycken et al. established a simple microwave-assisted de-sulfitative dimethylamination of 5-chloro-3-(phenylsulfanyl)-2-pyrazinones **24** utilizing DMF as a dimethylamine source and sodium carbonate as a necessary cofactor (Figure 17). The solvent solution for this reaction was DMF: H_2O at a ratio of 1:1, and the corresponding de-sulfitative aminated product **25** was produced in excellent yield. Finally, under improved circumstances, the applicability of this technology was tested on oxazinone instead of pyrazinones, and the intended products were generated in good yield.[47]

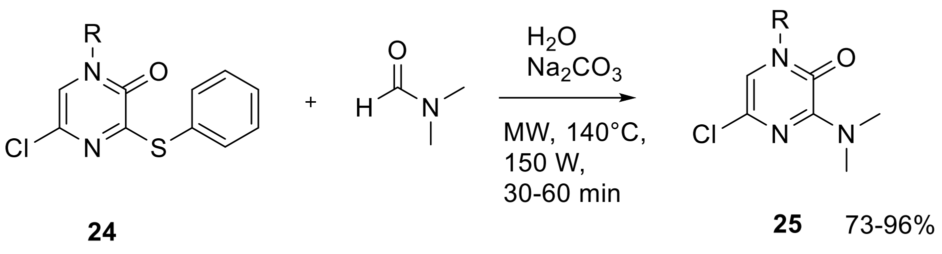


Figure 17. De-sulfitative amination of 2(1*H*)pyrazinone.

Hongting et al. discovered an efficient, atom-economic, and environmentally benign method for producing enamines **28** by intermolecular hydroamination of activated alkynes (Figure 18). At room temperature, the reaction was carried out in a solvent-free environment with a catalyst. Without producing any waste products, primary or secondary amines **27** were added to triple bonds **26**. DMF pretreatment with metal Na was utilized to synthesize (E)-ethyl-3-(dimethylamino)acrylate, and a new method for quinoline synthesis was presented.[48]

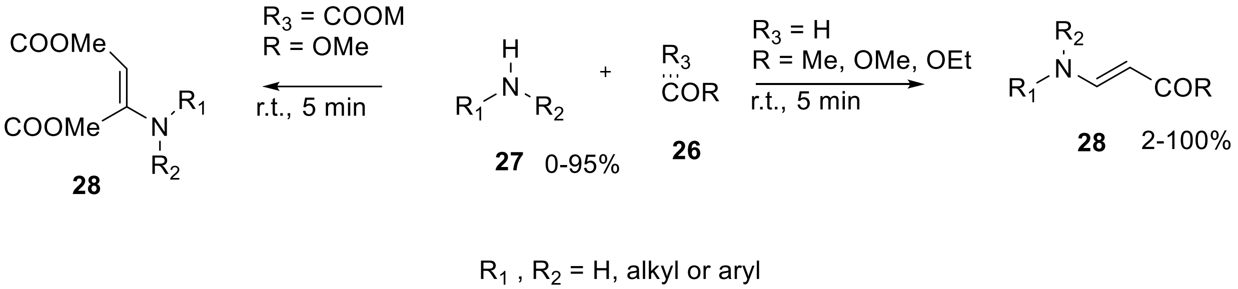


Figure 18. Intermolecular hydroamination of activated alkynes.

Li et al. devised a hypervalent iodine-mediated reaction between carboxylic acids **8** and *N,N*-dimethylformamide that occurs under moderate circumstances at ambient temperature to produce new O-aroyl-*N,N*-dimethyl hydroxyl amines **29** in high yields (Figure 19). The technique demonstrates strong functional group compatibility, as well as air and moisture endurance.[49]

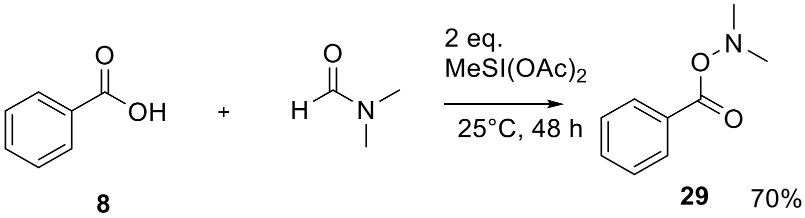


Figure 19. Synthesis of *O*-aroyl-*N,N*-dimethyl hydroxyl amines.

Liang and colleagues described a simple and effective one-pot multicomponent process using chalcones **30**, malononitrile **31**, and DMF in the presence of NaOH to produce functionalized 4-oxobutanamides **32** (γ-ketoamides) from simple, α, β-unsaturated enones (Figure 20). This reaction possesses a high atom economy, readily available starting materials, operational simplicity under mode rate circumstances, a broad substrate scope, and a high tolerance with various functional groups.[50]

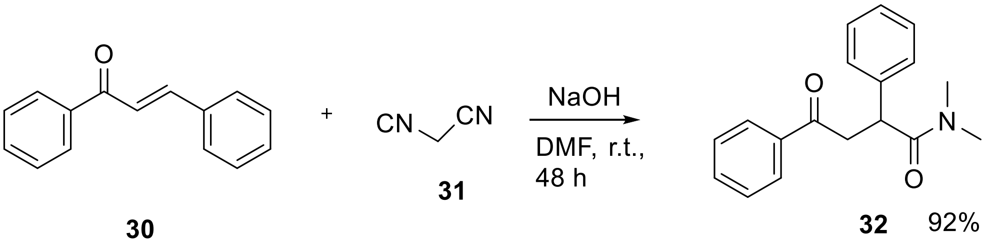


Figure 20. Synthesis of γ-ketoamide.

Xia and colleagues reported a facile and environmentally friendly method for synthesizing sulfonamides by t-BuOK-mediated direct S-N bond formation from sodium sulfonates **33** with formamides (Figure 21). This reaction takes place in a metal-free environment, and formamides are employed as an amine source. It avoids using pre-functionalized starting materials and provides an alternate approach for producing sulfonamides **34**.[51]

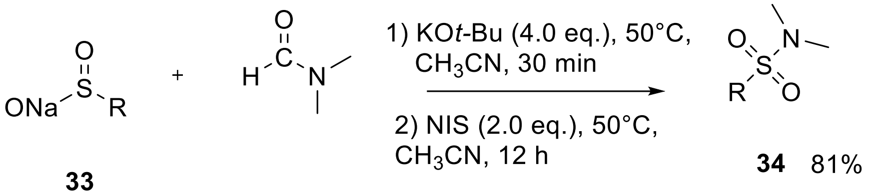


Figure 21. Synthesis of sulfonamides using DMF as an amine source.

Gong et al. described a base-promoted amination of aromatic halides **35** using a little quantity of N, N-dimethylformamide or amine as an amino source. Various aryl halides, including F, Cl, Br, and I, have been aminated effectively in good to outstanding yields (Figure 22).[52] This procedure is useful for industrial applications because of its ease of use and the unlimited availability of amino sources and aromatic halides.

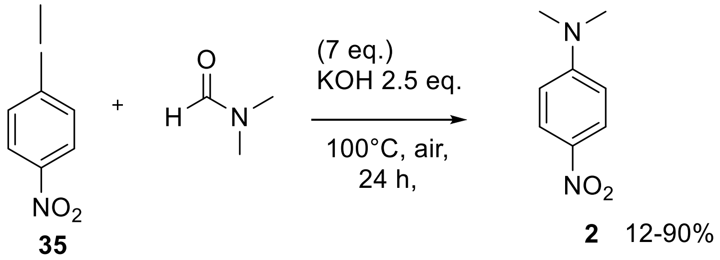


Figure 22. A base-promoted amination of aromatic halides.

4. DMF Mediated Methylenation Reactions

Several ways for employing DMF as a methylene source have recently been devised. Wang et al. created a novel technique for synthesizing vinyl quinolines **37** from methyl quinolines **36** (Figure 23) by employing DMF as a methylene source. The synthesis was accomplished using an iron-catalyzed sp^3 C-H functionalization followed by a C-N cleavage utilizing TBHP as a radical initiator. This approach is straightforward and efficient for producing many vinyl substituted quinoline derivatives with high yield. It also does not use organometallic compounds as reagents.[53]

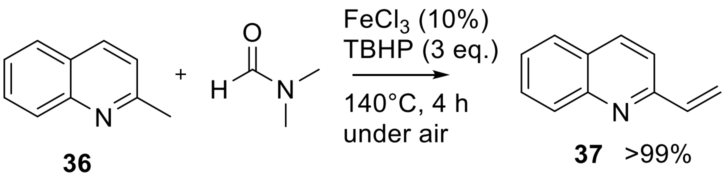


Figure 23. Synthesis of vinyl quinolones using DMF with iron catalyst.

Qian Xu and colleagues created an environmentally friendly iron-catalyzed benzylic vinylation that transfers the carbon atom in the N,N-dimethyl group from DMA or DMF to 2-methyl azaarenes **38** to make 2-vinyl azaarenes **39**. (Figure 24). The radical mechanism was used to carry out the reaction of N,N-dimethyl amides as one carbon source.[54]

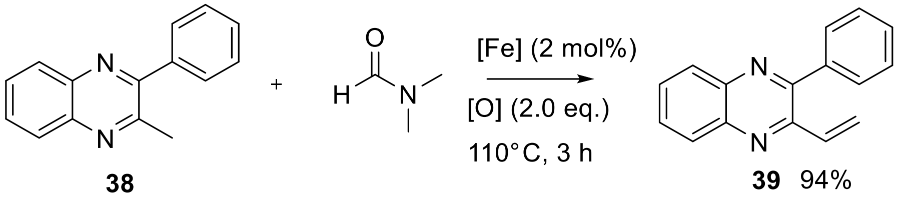


Figure 24. DMF Synthesis of vinyl 2-vinylazaarenes.

Miura et al. used copper as a catalyst to successfully α -methylenate benzyl pyridines **40**. The N-methyl group of DMA was used as the one-carbon source in the methylenation to develop α-styrylpyridine **41** derivatives (Figure 25), which are well known for their unique biological characteristics.[55]

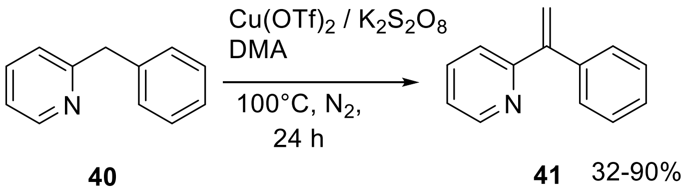


Figure 25. α-methylenation of benzylpyridines using DMA.

Using N,N-dimethylacetamides as a one-carbon source, Li et al. established an iron-catalyzed α-methylenation of aryl ketones **42** to generate, α, β-unsaturated carbonyl compounds (Figure 26). As an oxidant, potassium persulfate is utilized, and this approach is an effective synthetic method for the production of, α, β-unsaturated carbonyl compounds **43**.[56]

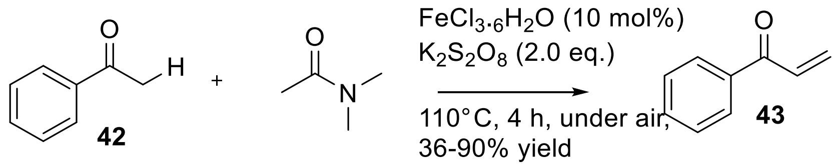


Figure 26. α-methylenation of acetophenones.

Wang et al. published a one-pot technique for the synthesis of 3-indolyl-3-methyl oxindoles **45** by C(sp^3)-H methylenation of 2-arylacetamides **44** utilizing DMF/Me_2NH-BH_3 as the methylene source. (Figure 27) [57]. Liu and colleagues described a technique for producing diindolylmethane **47** and its derivatives by copper catalyzed C-H activation of indole **46**, with DMF acting as a methylenating reagent. CuCl was primarily employed as a catalyst with strong regioselectivity, while TBHP was used as an oxidant. The process uses a commonly accessible copper catalyst and cheap DMF as a carbon source, and it works on a wide range of substrates under relatively moderate reaction conditions. (Figure 28).[58]

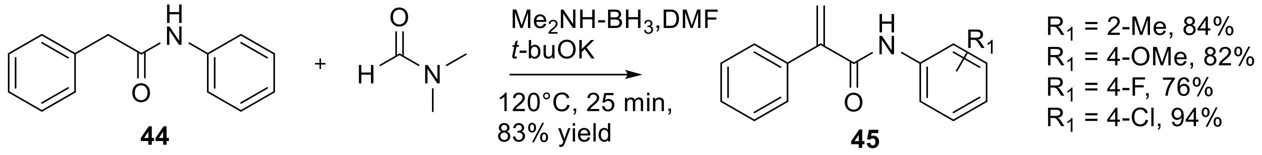


Figure 27. α-methylenation of 2-arylacetamides with DMF.

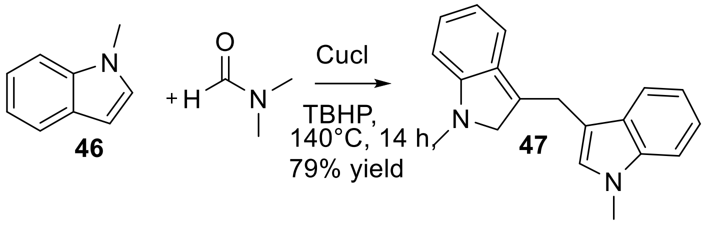


Figure 28. Cu-catalyzed synthesis of diindolylmethane.

Xue and colleagues produced methylation of ketones **7a** using DMF. Control experiment tests show that DMF serves dual purposes as a carbon supply for methylation and a hydrogen source in the rhodium-catalyzed reduction of methylene into a methyl group (Figure 29).[59]

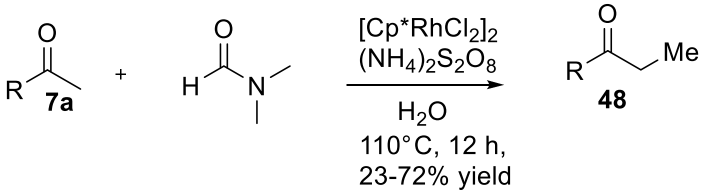


Figure 29. Rh-catalyzed direct methylation and hydrogenation of ketones using DMF.

A probable mechanism for methylation of ketone is depicted in Figure 30. Persulfate first oxidizes DMF to produce a reactive iminium intermediate. The intermediate **A** formed by enolate attack is transformed to intermediate **B**, which is then cleaved to form the unsaturated ketone intermediate **C**. Following that, the intermediate **C** is reduced, which is most likely formed by dehydrogenation with $[Cp^*RhCl2]_2$, resulting in the synthesis of methylated product **2C**.

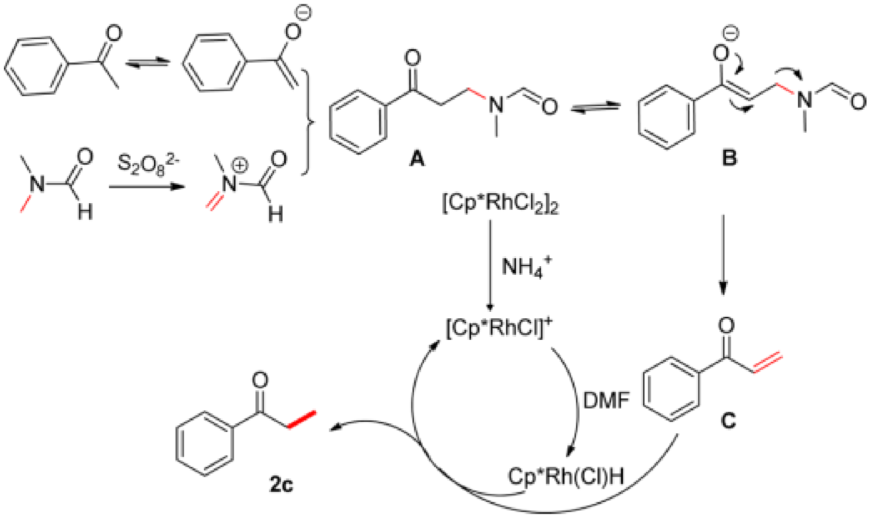


Figure 30. A possible mechanism for methylation and hydrogenation of ketone.

5. DMF Mediated Amidoalkylation Reactions

The α-amidoalkylation reaction has been extensively reviewed, and it involves the addition of carbon nucleophiles (primarily aromatic rings, alkenes, cyanides, isocyanides, alkynes, organometallic and active methylene-containing compounds) to substituted amides, where X is a leaving group (Figure 31).[60] The reactive intermediates in these reactions are N-acylimines **49** or N-acyliminium salts **50**. The higher electrophilicity of amidoalkylating reagents in comparison to those engaged in aminoalkylation reactions is the most essential property of their chemistry.

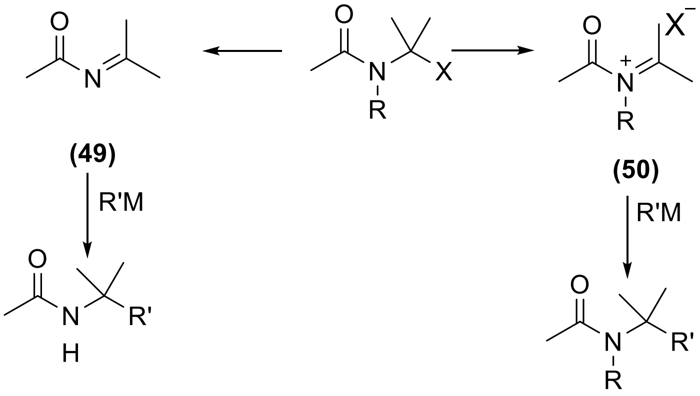


Figure 31. α-amidoalkylation reactions to form FC amidoalkylated product.

Li et al. described metal-free direct oxidative thiolation of a sp3 C-H bond adjacent to a nitrogen atom **52** using disulfides **51** for the synthesis of numerous N,S-containing compounds (Figure 32). Through the production of radical intermediates, the thiol group was effectively linked with the sp^3 C-H bond of N, N-dialkyl amides in this oxidative thiolation process in the presence of TBHP/Molecular sieves.

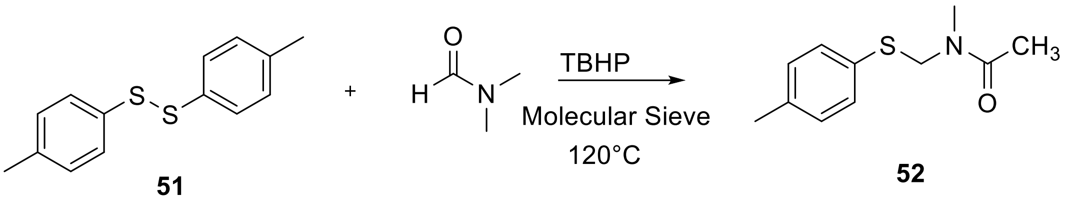


Figure 32. Thiolation of sp^3 C-H bond next to a nitrogen atom.

This technology may also be used to produce several benzothiazole **54** and fipronil analogues (Figure 33).[61] Stephenson et al. used thermolysis and oxidative photocatalysis to create Friedel-Craft (FC) amidoalkylation of alcohols and electron-rich arenes as a powerful nucleophile with alkyl amides 1b (Figure 34). The FC amidoalkylated product **53** was synthesized by oxidizing N,N-dialkyl amides with persulfate and a photocatalyst. Persulfate at 55°C, on the other hand, provides amidoalkylated product. Persulfate was utilized as an affordable and efficient oxidant in this procedure for the formation of C-O and C-C bonds. When compared to thermolytic reaction conditions, light catalysis offered superior selectivity and yields for Friedel-Crafts reactions most of the time.[62]

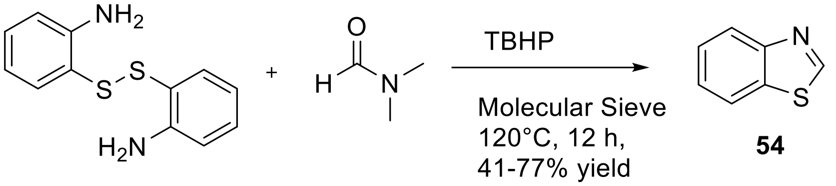


Figure 33. TBHP-mediated synthesis of benzothiazoles.

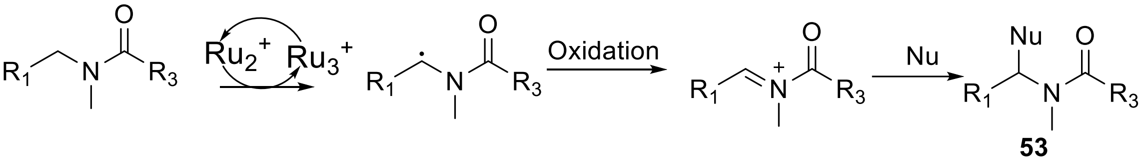


Figure 34. FC amidoalkylation using alkyl amides.

Li et al. developed a transition metal-free approach for amidation of the sp^3 C-H bond in amides employing iodide anion as a catalyst and TBHP as an oxidant (Figure 35). It proceeds by free radical intermediation, as proven by TEMPO, and the result has the potential for bioactivity **56**. Because of the moderate temperatures and easily accessible chemicals, this is an effective approach for direct C-N bond synthesis.[63]

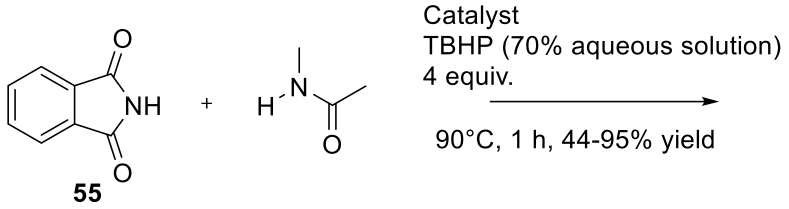


Figure 35. Amidoalkylation under metal free condition using DMA.

Chen and colleagues showed copper-catalyzed C-N bond synthesis of triazoles in 2017 via cross dehydrogenative coupling of NH-1,2,3-triazoles **57** with N,N-dialkylamides to create N-amidoalkylated triazoles **58** (Figure 36). When the reaction was carried out using 4-aryl-substituted NH-1,2,3-triazoles, the expected N2-substituted 1,2,3-triazoles were produced, as well as a tiny quantity of N1. This approach is effective for the selective synthesis of N2-substituted 1,2,3-triazoles.[64]

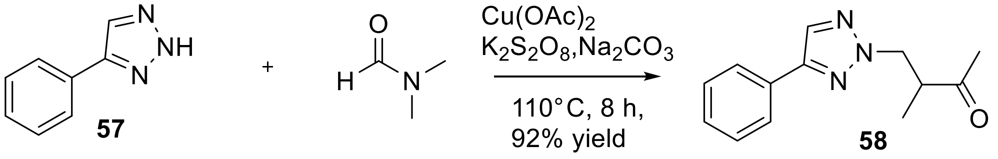


Figure 36. Copper-catalyzed C-N bond formation of triazoles.

Zhu and colleagues developed a novel technique for synthesizing 2-amidoalkylated benzothiazole and 3-amidoalkyl modified indolinone derivatives under metal-free conditions utilizing N, N-dialkylamides and potassium persulfate as oxidants (Figure 37). Using simple N,N-dialkyl amides, including formamides, the appropriate amidoalkylation products were produced selectively.[65]

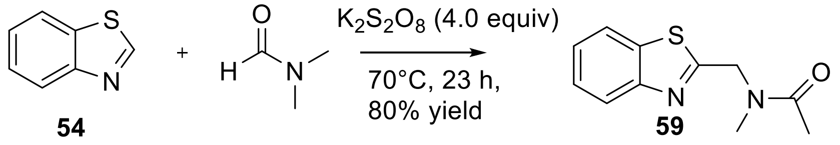


Figure 37. Amidoalkylation of benzothiazoles with DMA.

6. DMF Mediated Cyanation Reactions

The cyanation of Csp^3-H bonds next to N atoms in tertiary amines is an essential technique for producing -amino nitriles, which are flexible precursors of amino acids with a wide range of applications in biochemistry and medicine. It is worth noting that dialkylamides can undergo reaction to form cyano groups. Ding et al. (2011) reported a novel and different type of pathway to produce aryl nitriles via Pd-catalyzed cyanation of indoles **46** and benzofurans via functionalization of the C-H bond using DMF as a source of CN, and control experiments revealed that N and C of the cyano group are generated from DMF.[66]

Similarly, in 2015, Chen and co-workers developed a selective copper-catalyzed C_3-cyanation of indole under an oxygen atmosphere with DMF as a safe CN source and as a solvent (Figure 38).[67]

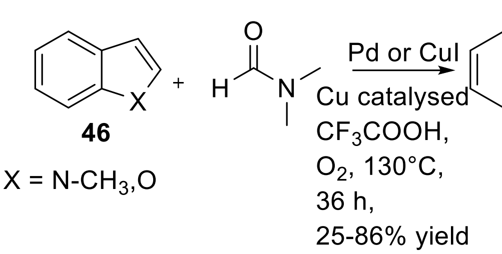


Figure 38. Cyanation of indole and benzofuran.

Wang et al. performed copper catalyzed cyanation of indoles with DMF as a single CN surrogate (Figure 39). Aryl nitriles can be synthesized from electron-rich arenes and aryl aldehydes. The main intermediary in this reaction is acyl aldehydes. This reaction's process required C-H activation with the assistance of a copper catalyst, followed by carbonylation. Because of its usefulness in the medical area, particularly in the creation of therapeutic oestrogen receptor ligands, 3-cyanoindoles have drawn a lot of attention.[68]

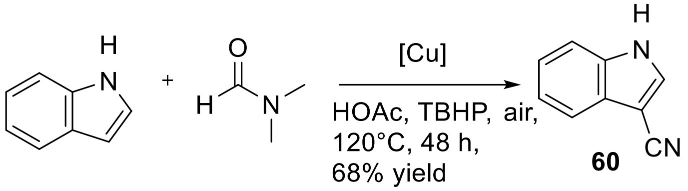


Figure 39. Cyanation of indole with DMF.

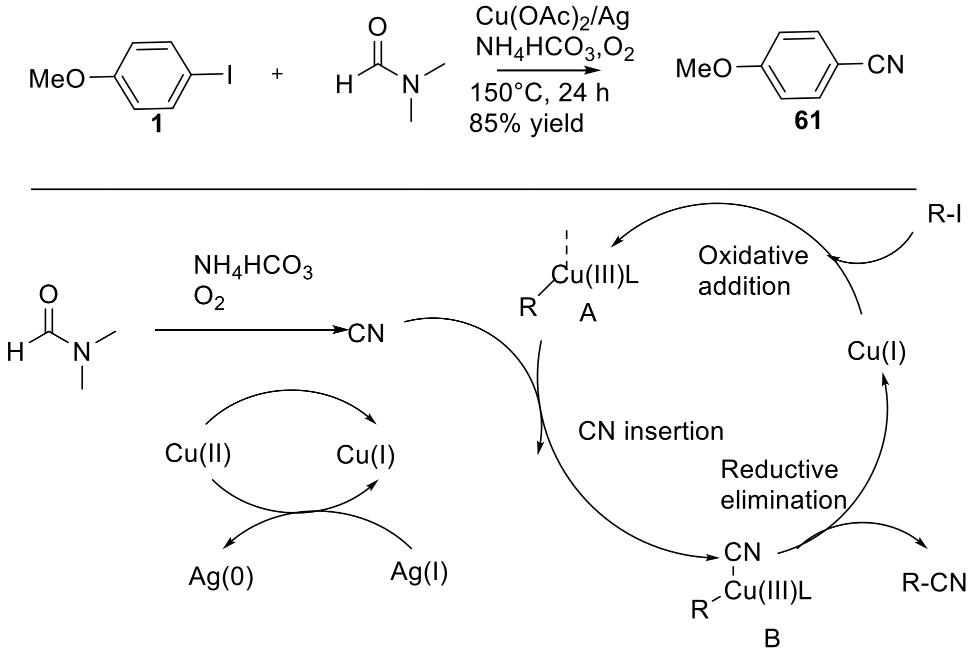


Figure 40. Cyanation of arylhalides and plausible mechanism.

Chang et al. proposed a novel method for synthesizing Aryl nitriles **62**. Cyanation of aryl halides **1** catalyzed by copper acetate and Ag as oxidants, using ammonium bicarbonate as a N supply and DMF as a C source for the cyanide functional group (Figure 40). Regarding the critical roles of Cu (II) species in the in-situ production of CN units and subsequent cyanation of aryl halides, Ag_2CO_3 re-oxidizes the resulting Cu(I) species under copper-catalyzed oxidative conditions. This process is feasible and safe, and it produces nitriles in moderate to excellent yields.[69]

Ushijima et al. synthesized aromatic nitriles **62** from electron-rich aromatics in a metal-free one-pot process. When molecular iodine in aqueous ammonia is combined with $POCl_3$ and DMF (Figure 41). Figure 41 depicts a probable mechanism for this process. The aromatic imine can be produced by treating the iminium salt with ammonia. The aromatic imine is next oxidized by molecular iodine, which produces the aromatic N-iodoimine, which is then eliminated in aqueous ammonia to produce the aromatic nitrile.[70]

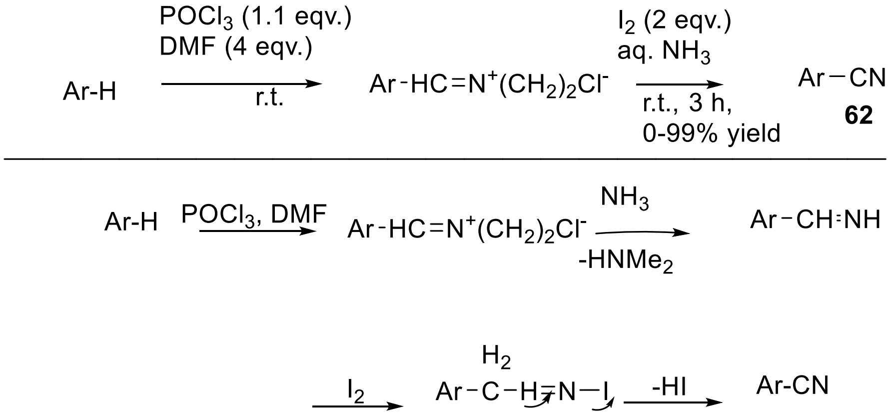


Figure 41. Conversion of electron-rich aromatics into aromatic nitriles.

The requirement for extremely electron-rich aromatics in the production of aromatic N, N-dimethyl iminium salts, on the other hand, limits the breadth of this transition. As a result, the writers should devise more user-friendly approaches for this change. Following this, they developed a unique one-pot approach for preparing aromatic nitriles from aryl bromides and arenes by forming aryl lithium and their DMF adducts (Figure 42).[71] The treatment with molecular iodine in aqueous ammonia was then performed. Similarly, in the presence of Mg, the same author reported the synthesis of aryl nitriles from aryl bromides.[72]

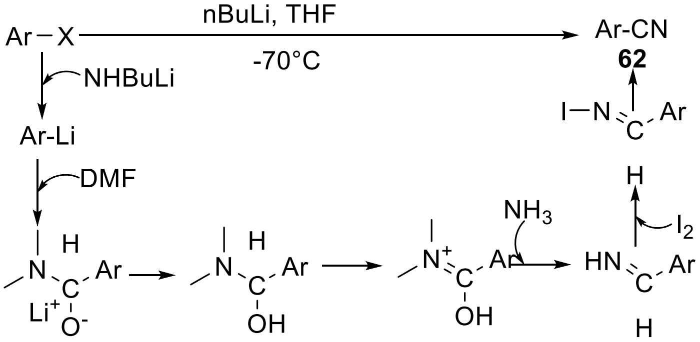


Figure 42. Conversion of electron-rich aromatics into aromatic nitriles and plausible mechanism.

7. DMF Mediated Formylation Reactions

DMF is used as a reagent in a variety of significant chemical processes, including the Vilsmeier-Haack reaction, which results in the formylation of aromatic, non-aromatic, and heteroaromatic compounds. Dialkylamides were also employed as a source of formylation. Wang et al. transformylated various amines, primary or secondary, aromatic or alkyl cyclic or linear, mono- or di-amine with DMF as a formylation reagent to obtain corresponding formamides with CeO_2 catalyst. The reaction does not require any homogeneous acidic or basic additives and is water tolerant. The CeO_2 catalyst's high basicity and medium water-tolerant acidity (Figure 43) are its finest features.[73]

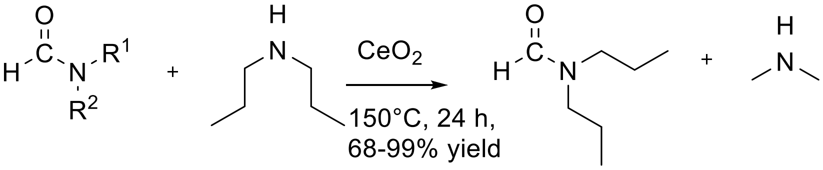


Figure 43. Trans formylation of amines with DMF.

In 2017, Jagtap and colleagues reported extremely effective Ni(II) metal complex catalysing N-formylation **63** and N-acylation **64** of amines in the presence of imidazole at 150°C in a homogeneous medium utilizing N,N-dimethylformamide and *N,N*-dimethylacetamide as acyl sources (CHO) (Figure 44).[74] It has a wide substrate range that includes aliphatic, aromatic, and heterocyclic molecules.

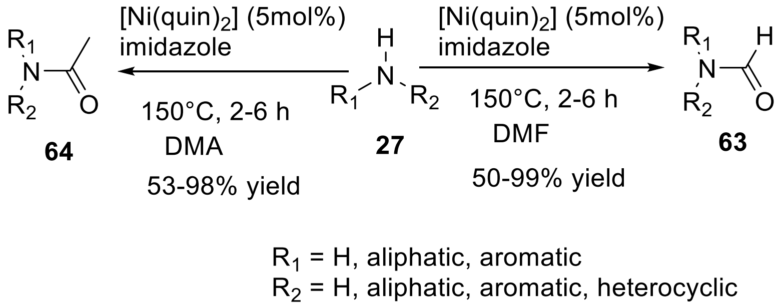


Figure 44. Formylation and acylation of amines using N,N-dialkylamides.

The significance of these reactions is their low cost, readily available starting material, strong reactivity, and inertness to air and water [86]. Larsen et al. discovered a simple process for synthesizing, α, β-acetylenic aldehydes **66**, acetylides, which are then converted to lithium acetylides using n-BuLi (Figure 58). Formylation of lithium acetylides was completed in the presence of DMF, followed by α-aminoalkoxide with 10% aqueous KH_2PO_4 to obtain the desired product.[75] (Figure 45)

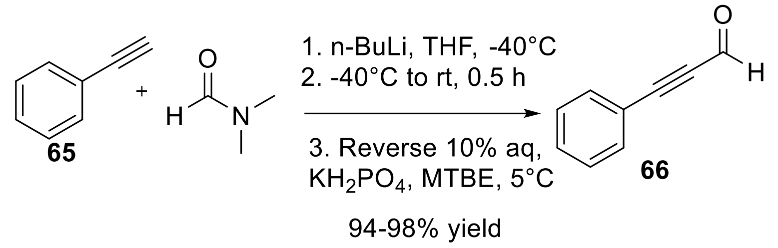


Figure 45. Synthesis of α, β-acetylenic aldehydes.

Under microwave irradiation, Jeon and colleagues observed that methyl benzoate **67** enhanced N-formylation of several primary and secondary amines **69** using DMF as a formylating agent (Figure 46). The primary benefit of this approach is selective N-formylation in the presence of a hydroxyl group.[76]

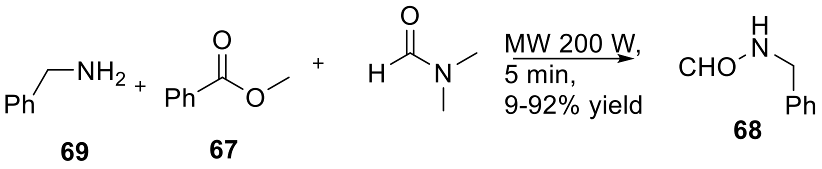


Figure 46. N-formylation of various 1° and 2° amines.

8. DMF Assisted Hydrogenation Reactions

Dialkylamides can operate as a hydrogen source and have been employed in a variety of functional group transformations. It is preferable to employ hydrogen gas produced in situ from dialkylamides rather than handling easily combustible hydrogen gas.

Hua et al. described a triruthenium dodecacarbonyl [$Ru_3(CO)_{12}$] catalyzed stereo divergent semi-hydrogenation of diaryl alkynes **70** using *N,N*-dimethylformamide/water as the hydrogen source to produce cis-**71** and trans **72**-stilbenes (Figure 47). When HOAc was employed, excellent stereoselectivity in favour of cis-product production was found. Surprisingly, the stereochemical preference shifted to the trans-isomer, with TFA acting as an additive. This method is excellent for synthesizing natural product analogues such as cis-combretastatin A-4 and trans-resveratrol.[77]

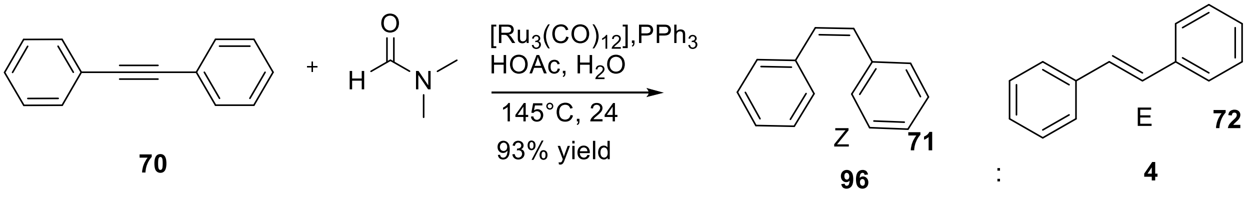
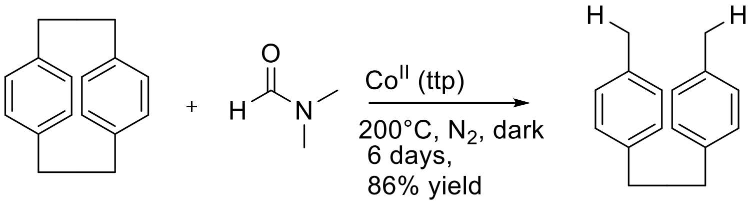


Figure 47. Stereo divergent [$Ru_3(CO)_{12}$] catalyzed semi hydrogenation of diaryl alkynes.

Chan et al. described a cobalt porphyrin-catalyzed hydrogenation process that hydrogenated the C-C bond of [2.2] para cyclophane **73** (PCP) utilizing DMF as a solvent and hydrogen atom transfer agent (Figure 48). The C-C sigma bond of PCP is attacked by metallo radical Co (II) porphyrins, and the resulting benzyl radical removes a hydrogen atom from DMF to provide the hydrogenated product **74**. The presence of benzyl radical intermediates in undergoing hydrogen atom transfer from DMF was indicated by the results of several control experiments.[78]

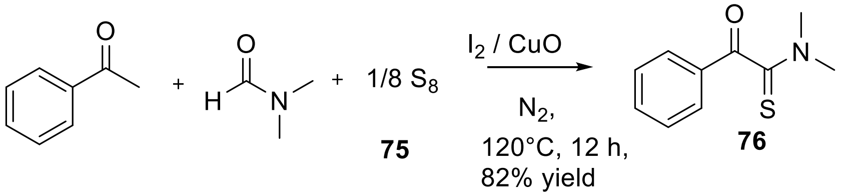


73

74

Figure 48. DMF as hydrogenating reagent for benzylic positions.

In 2017, Liu and co-workers used a copper oxide and iodine-mediated direct redox method to synthesize α-arylketothioamides **76** from acetophenones, elemental sulphur **75**, and DMF in a nitrogen environment (Figure 49). Sulphur acts as a nucleophilic building block, while DMF acts as a solvent and an amino group supply (dimethylamine). This redox-efficient reaction tolerated a wide range of functional groups.[79]



75

76

Figure 49. Synthesis of α-arylketothioamides.

9. DMF Mediated Carbonylation Reactions

Carbonylation is another important process that, in the presence of adequate catalysts, creates the lethal "CO" gas from dialkylamides. As a result, carbonylation with dialkylamides is quite advantageous. Gunanathan and colleagues developed a unique bond activation approach for the efficient synthesis of simple and functionalized symmetrical and unsymmetrical urea derivatives from amines with DMF as the CO source (Figure 50). Ruthenium pincer complex stimulates amine N-H bonds, which results in CO insertion from DMF and hydrogen release. Amine nucleophilicity is essential for urea synthesis. This reaction is noteworthy because it occurs in an open state, produces no side products, and requires no pressure adjustment.[80]

Furthermore, Chen and colleagues discovered a unique and highly effective method for synthesizing imidazolinones **78** from carbene complexes **77** using an oxygen atom insertion procedure of NHC copper complexes in the presence of DMF as an oxygen source (Figure 51).[81]

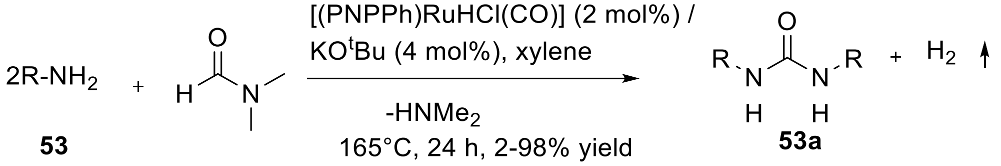


Figure 50. Carbonylation of amines with DMF.

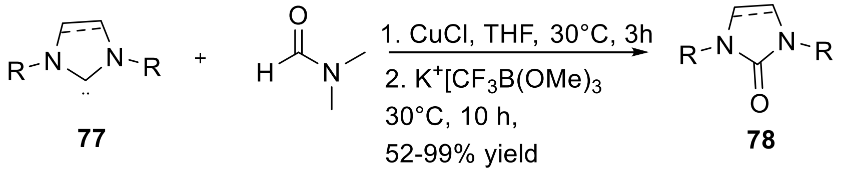


Figure 51. Formation of complicated imidazolinones with DMF.

Conclusions

DMF/DMA can be particularly used in synthesizing functionalized carbo- and heterocyclic compounds to design novel, highly effective fine-chemicals, and broad-spectrum pharmaceuticals. With the introduction of novel reagents and catalytic systems, as well as the need to design efficient synthesis methods, dialkylamide is expected to find new uses in organic synthesis. Diakyl amides have mostly been employed as a synthetic agents by monomerizing one of the groups. Furthermore, it is more likely to be used as a difunctionalizing agent, as an alkyl group connected to the carbonyl and nitrogen in DMA can be functionalized at both ends at the same time. Dialkyl amides will continue to attract the interest of synthetic chemists as a synthon, ligand, dehydrating agent, and solvent due to their low cost, accessible availability, and versatility in reactivity. We thank all the writers cited here for their significant contributions to the advancement of this discipline. We hope that it is sufficiently impressive and thorough that it will enhance the interest of organic chemists, and spark further research into the applications of DMF/DMA beyond being just a polar solvent, because it can be used as a substrate in a variety of reactions such as formylation, amination, amidoalkylation, aminocarbonylation, amidation, and cyanation under both metal-catalyzed and metal-free conditions. We believe this review will make it easy for the synthetic chemists and invoke an idea about utility of dialkyl amides.

Conflict of interest

The authors declare no conflict of interest or any funding/support that could have affected the results presented in the work. On behalf of all authors, the corresponding author states that there is no conflict of interest.

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