Tetrahedron 65 (2009) 8313–8323

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Tetrahedron report number 885

N,*N*-Dimethylformamide: much more than a solvent

Jacques Muzart *

Institut de Chimie Moléculaire de Reims, UMR 6229, CNRS—Université de Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cedex 2, France

ARTICLE INFO

Article history:
Received 8 June 2009
Available online 27 June 2009

Keywords:
N,*N*-Dimethylformamide
DMF
Carbonylation
Amidation
Aminocarbonylation
Formylation
Dehydration
Reduction
Cycloaddition
Catalysis

Contents

1. Introduction

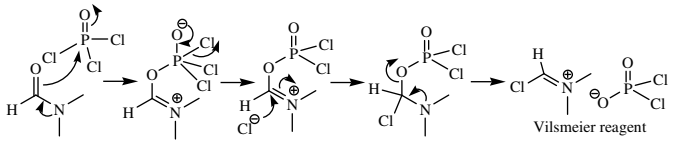
N,*N*-Dimethylformamide (DMF) is an excellent polar solvent for various classes of compounds, the dissolution being favoured by interactions of the substrate with DMF. In the case of metallic compounds, DMF can be, furthermore, an effective ligand[1] which can even substitute coordinated PPh_3,[2] its O-atom acting as donor.[3,4] Besides, DMF can react as either an electrophilic or

Abbreviations: Bn, CH_2Ph; Bz, COPh; cat., catalytic; dba, dibenzylidene acetone; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; dppe, 1,2-bis(diphenylphosphino)ethane; dppf, 1,1′-bis(diphenylphosphino)ferrocene; equiv, equivalent; Ms, SO_2Me; MW, microwave irradiation; NBoc, NCO_2t-Bu; NCbz, $NCOCH_2Ph$; rt, room temperature; TMEDA, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; TMS, $SiMe_3$; tol, tolyl; Ts, SO_2(*p*-MeC_6H_4).

* Tel.: +33 3 2691 3237; fax: +33 3 2691 3166.
E-mail address: jacques.muzart@univ-reims.fr

0040-4020/$ – see front matter
doi:10.1016/j.tet.2009.06.091

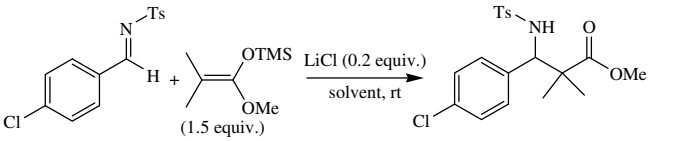
a nucleophilic agent, and, in addition, can be the source of various key intermediates mediating reactions. The aim of this review, which is not exhaustive, is to highlight different roles of DMF in organic synthesis, organometallic chemistry and catalysis. This review will not, however, survey the processes that require the prerequisite formation of a reagent by the reaction of DMF with halides, the most commonly used being the Vilsmeier reagent obtained from the combination of DMF with $POCl_3$ (Scheme 1).[5] Indeed, the different reactions carried out using the powerful Vilsmeier-type reagents are well documented in several reviews.[6]



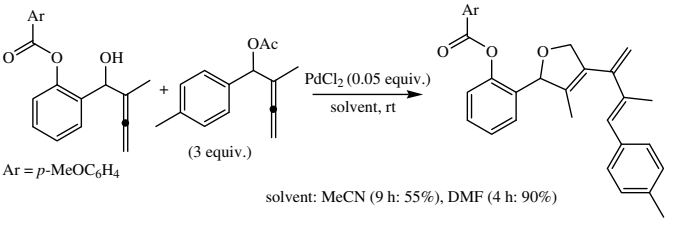
Scheme 1.

2. Influence on equilibria and reaction courses

The solvent effect of DMF on the efficiency[7–9] (Eqs. 1[8] and 2[9]), rate[10,11] and mechanism of reactions,[12] and on the solvation of anions has been reviewed by Parker forty years ago.[13]

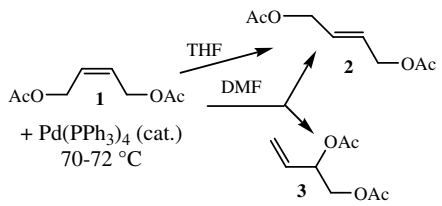


(1)

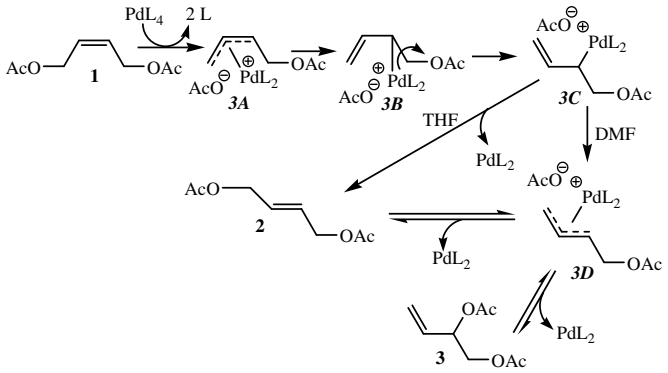


(2)

The team of Amatore and Jutand has carried out a lot of studies concerning the behaviour of Pd complexes in DMF.[14] They have demonstrated that, for the cationic η^3-allylpalladium complex formed from allyl acetate and Pd^0, the acetate anion sticks on Pd^{II} in THF, while it is located far from Pd^{II} in DMF.[15] This observation has been the key to rationalize the unexpected solvent effect on the Pd^0-catalysed isomerisation of (*Z*)-1,4-diacetoxy-2-butene (**1**), i.e., the formation of the *E*-isomer (**2**) in THF, while **2** and 1,2-diacetoxy-3-butene (**3**) are simultaneously produced in DMF (Scheme 2).[16] These isomerisations involve, in both solvents, the η^3-allylpalladium **3A** and the η^1-allylpalladiums **3B** and **3C** (Scheme 3). From **3C**, the proximity, in THF, of the acetate anion to the allyl moiety allows its easy addition leading to **2**. In contrast,

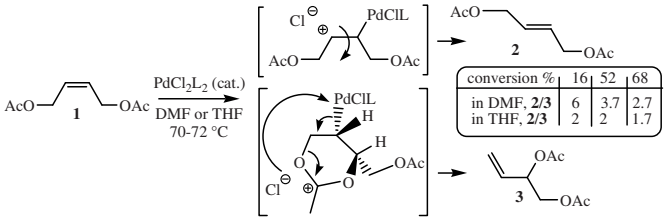


Scheme 2.



Scheme 3.

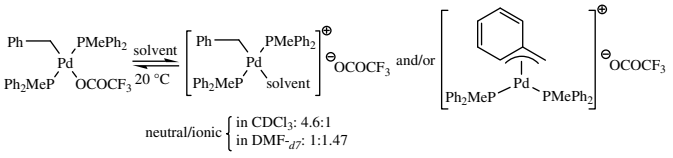
the remoteness of the acetate anion in DMF permits the competitive transformation of **3C** into the η^3-allylpalladium intermediate **3D** that evolves into both **2** and **3**. Although the mechanism of the Pd^{II}-catalysed isomerisation of allylic acetates is different, a solvent-dependent reactivity of **1** under Pd^{II} catalysis has also been observed (Scheme 4).[10]



Scheme 4.

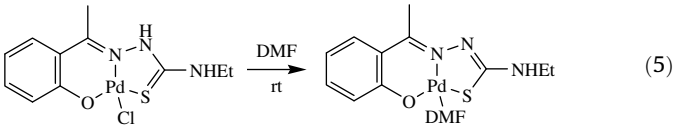
In studying the reaction of *n*-Bu_4NCl with $PdCl_2(PPh_3)_2$, leading to the anionic complex shown in Eq. 3, the Amatore/Jutand team has shown that the substitution of PPh_3 by the chloride anion is more efficient in THF than in DMF. According to the authors, this is 'probably due to the lower capacity of THF relative to DMF to solvate chloride ions, compared to the larger anionic species PdX_3L^-'.[17] The formation of cationic complexes is also favoured in DMF, as exemplified by the solvent-dependent equilibrium between neutral and ionic benzylpalladium complexes depicted in Eq. 4.[18,19]

$$PdCl_2(PPh_3)_2 + n\text{-}Bu_4NCl \rightleftharpoons [PdCl_3(PPh_3)]^{\ominus}[n\text{-}Bu_4N]^{\oplus} + PPh_3 \quad (3)$$



(4)

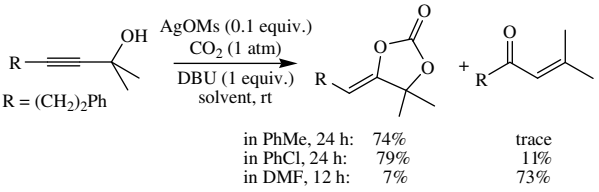
Kovala-Demertzi et al. have disclosed the DMF-promoted elimination of HCl from the complex shown in Eq. 5.[20]



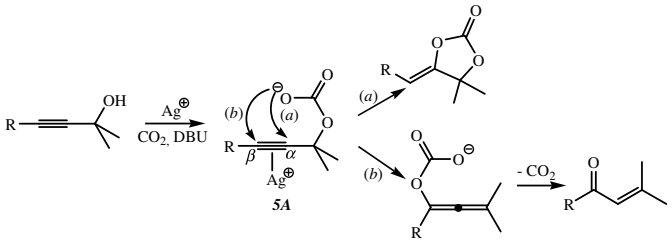
(5)

The solvent-dependent course of an Ag^I-catalysed reaction is illustrated in Eq. 6. The main product obtained from propargylic alcohols under a carbon dioxide atmosphere and basic conditions is a carbonate in toluene or chlorobenzene, and an enone in DMF.[21] According to Yamada's team,[21] the ionic intermediate **5A** (Scheme 5)

would have, in a polar solvent, an elongated C-O$^-$ bond, enhancing the attack on the β-carbon (path *b*) to the detriment of the cyclic carbonate (path *a*). This [3,3]-sigmatropic rearrangement is followed by the release of CO_2, resulting in the formation of the enone.

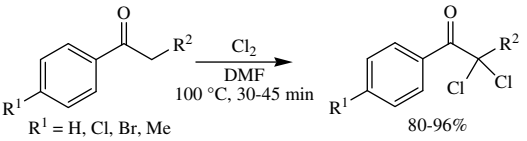


(6)

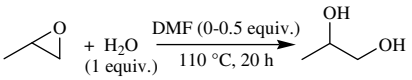


Scheme 5.

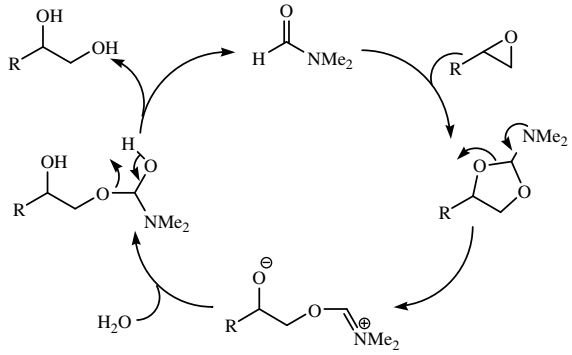
According to De Kimpe et al., the bis-α-chlorination of aromatic ketones shown in Eq. 7 is due to catalysis by DMF.[22] DMF also catalyses the hydrolysis of epoxides (Eq. 8) via, according to Jiang et al., the formation of *N*,*N*-dimethylformamide ethylene acetal derivatives (Scheme 6).[23] The decisive role of DMF for the glycosidation of 2,3,4-triacetyl-1-bromo-α-D-xylopyranose with various terpenols (Eq. 9)[24] would involve the Vilsmeier–Haack-type intermediate depicted in Scheme 7.[25]



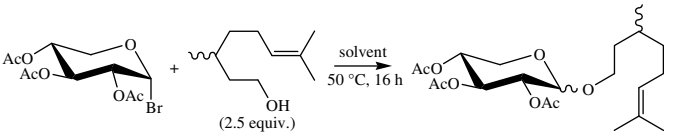
(7)



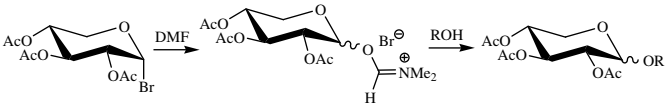
(8)



Scheme 6.

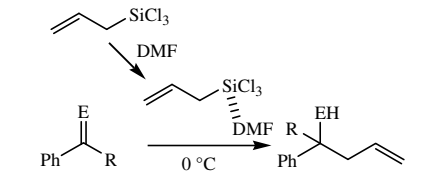


(9)



Scheme 7.

Kobayashi et al. have accomplished the highly effective synthesis, in DMF, of homoallylic alcohols and amines, based on the addition of allylic trichlorosilanes to either aldehydes[26] or *N*-benzoylhydrazones[27–29] and *N*-(*o*-hydroxyphenyl)imines.[30] The process was then extended to the allylation of *N*-Boc and *N*-Cbz imines.[31] According to the authors, the reaction is promoted by coordination of the silane to DMF to form a hypervalent silicate that is reactive towards electrophiles (Scheme 8).[29,31]



Scheme 8.

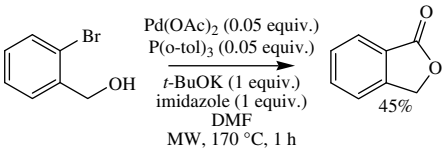
3. Source of carbon monoxide[†]

DMF decomposes slightly at its boiling point to afford dimethylamine and carbon monoxide, this reaction occurring even at room temperature in the presence of some acidic or basic materials.[32] This observation has led to the use of DMF as a carbonylating agent.

Refluxing a DMF solution of $RhCl_3$ and PPh_3 for 1 h leads to the formation of $RhCl(CO)(PPh_3)_2$.[33] At room temperature in the absence of the phosphine, the concomitant decrease in the oxidation state is not observed and the cationic complex $[RhCl_2(DMF)_4]Cl$ is produced[34] while heating yields $[RhCl_2(CO)_2][NH_2Me_2]$.[35] Carbonyl complexes have also been obtained from the reaction of Ir, Ru and Pt halides with DMF.[34,35] $RuHCl(P\textit{i}\text{-}Pr_3)_2]_2$ yields, at room temperature, $Ru(H)_2Cl(P\textit{i}\text{-}Pr_3)_2(\eta^2\text{-}OCNMe_2)$, the heating of which at 80 °C affords DMF, $HNMe_2$, $RuHCl(CO)(P\textit{i}\text{-}Pr_3)_2$, $RuH(H_2)Cl(P\textit{i}\text{-}Pr_3)_2$ and $RuHCl(CNMe)(P\textit{i}\text{-}Pr_3)_2$.[36]

In contrast to the above salts, no carbonylpalladium species can be synthesised in this way, refluxing $PdCl_2$ or Na_2PdCl_6 in DMF leading to the rapid formation of colloidal palladium suspensions.[34] In fact, it is known that CO can reduce Pd^{II} into Pd^0.[37]

Alterman et al. have used DMF as the carbon monoxide source, for the Pd^0-catalysed synthesis, under microwave irradiation, of phthalide from 2-bromobenzyl alcohol (Eq. 10). Under these conditions, the major side product was the debrominated benzyl alcohol (see Section 6).[38]

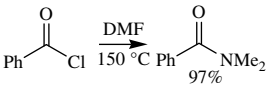


(10)

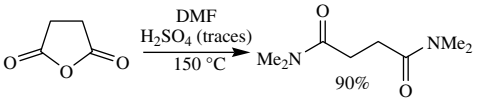
4. Source of Me_2N unit

Heating DMF solutions of acid chlorides (Eq. 11),[39] esters[40] or anhydrides, possibly in the presence of traces of a mineral acid (Eq. 12),[39] affords the corresponding amides. It has been proposed that

[†] See also Scheme 13.



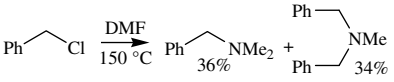
(11)



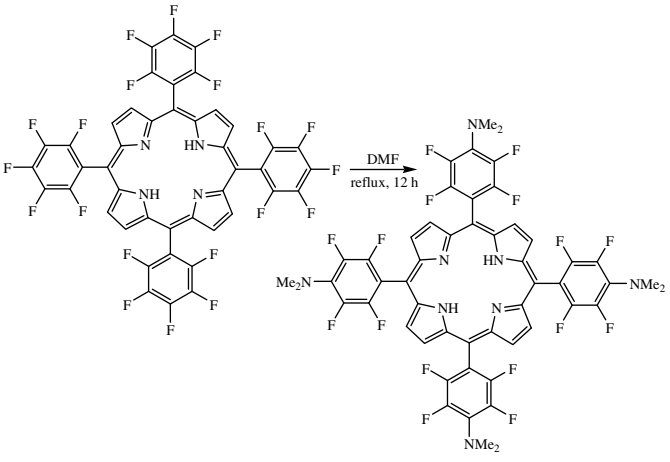
(12)

the reaction of acid chlorides, that only requires heating, involves the attack of the acyl group by the nitrogen atom of DMF.[41]

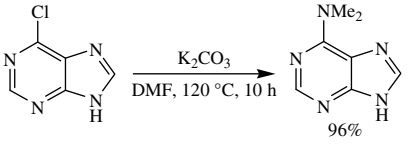
Substitution reactions of aryl halides leading to amines (Eqs. 13,[39] 14[42] and 15[43])[44,45] and desulfitative dimethylamination of 5-chloro-3-(phenylsulfanyl)pyrazin-2-(1*H*)-ones (Eq. 16[46]) have been carried out using DMF as the solvent and reactant. The formation of the dimethylamino compounds would involve the reaction of the substrate with either DMF followed by loss of carbon monoxide (Scheme 9, path *a*),[43,45,46] or with dimethylamine formed from the decomposition of DMF (path *b*).[46]



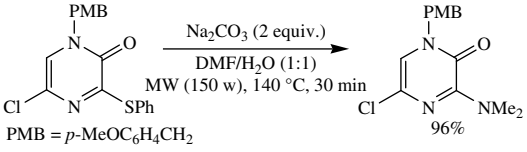
(13)



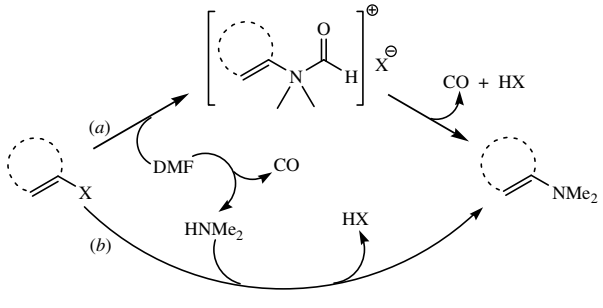
(14)



(15)

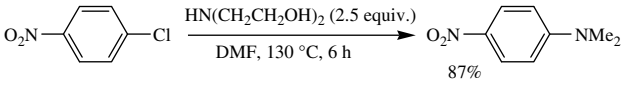


(16)

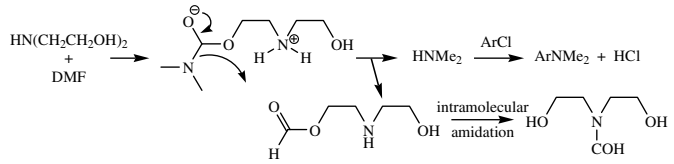


Scheme 9.

The promotion of the dimethylamination of activated aromatic halides by diethanolamine has been reported (Eq. 17).[47] In this case, the in situ formation of a DMF/$HN(CH_2CH_2OH)_2$ adduct was supported by the production of *N*,*N*-bis(2-hydroxyethyl)formamide (Scheme 10).

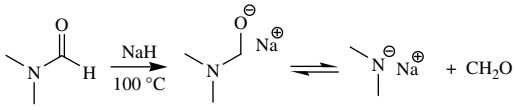


(17)



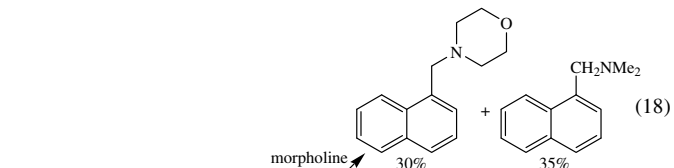
Scheme 10.

According to Nasipuri et al., the NaH-mediated decomposition of DMF produces sodium dimethylamide and formaldehyde as depicted in Scheme 11.[48] No appreciable gas evolution has been observed even after addition of water. This observation contrasts with a prior proposal from Powers et al. who have suggested the formation of carbon monoxide and hydrogen instead of formaldehyde.[49] Paul and Schmidt have considered that the cleavage of *t*-butyl esters with NaH in DMF is mediated by sodium dimethylamide,[50] but, according to a subsequent report from Lloyd-Jones et al., this reaction would rather involve sodium hydroxide formed from NaH and traces of water.[51] At this level, it is necessary to point out that mixtures of NaH and DMF can undergo dangerous uncontrollable exothermic decomposition.[51]

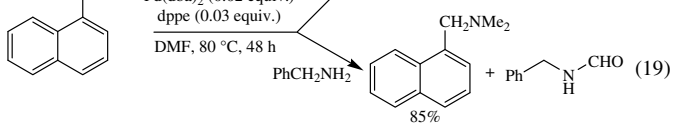


Scheme 11.

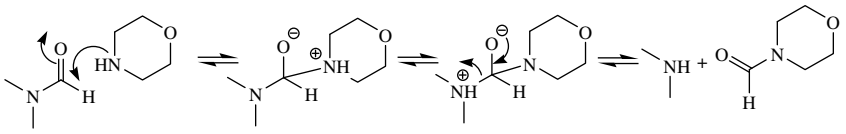
In studying the nucleophilic addition, in DMF, of morpholine on η^3-benzylpalladium intermediates, Fiaud et al. observed the concomitant formation of the *N*,*N*-dimethyl adduct (Eq. 18).[52] As this compound was not observed in the absence of morpholine, the reaction of this latter base with DMF, leading to its in-situ formylation and production of dimethylamine, has been postulated (Scheme 12). This agrees with the formation of *N*-benzylformamide, as by-product, when benzylamine was used instead of morpholine (Eq. 19).[52]



(18)

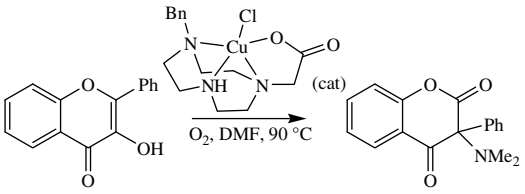


(19)



Scheme 12.

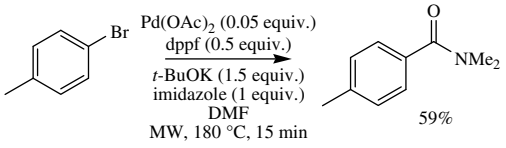
Recently, Chavez et al. have reported the incorporation of the NMe_2 fragment, possibly via a radical process, in the course of the Cu-catalysed oxidation of 3-hydroxyflavone by oxygen (Eq. 20).[53,54] Using $^{18}O_2$ and $H_2{}^{18}O$ experiments, the oxygen atoms of the isolated compound are found to be from the starting substrate.[53]



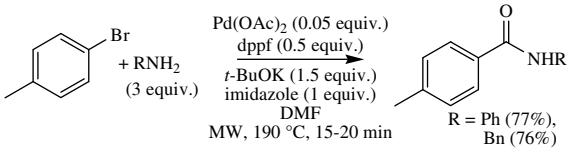
(20)

5. Source of Me_2NCO unit

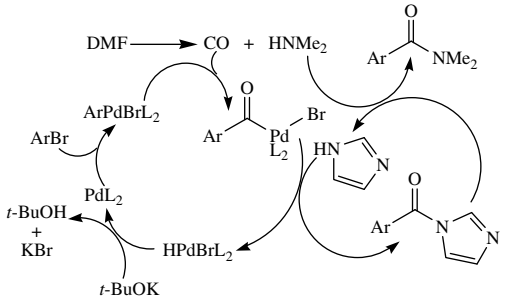
Hallberg et al. have used DMF to accomplish the Pd-catalysed aminocarbonylation of aryl bromides under microwave irradiation. In the presence of *t*-BuOK and imidazole, 4-bromotoluene is, thus, transformed into the corresponding dimethylamide (Eq. 21).[55] When carried out in the presence of an excess of an amine such as benzylamine, the reaction affords the aryl benzylamide (Eq. 22). According to the proposed mechanism (Scheme 13), the formation of the dimethylamide involves carbon monoxide and then dimethylamine, both produced from DMF decomposition.



(21)



(22)



Scheme 13.

6. Source of reducing agents

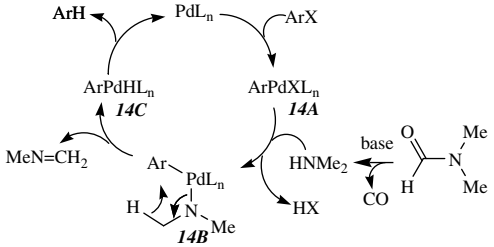
A few examples of the reduction of metal salts mediated by the DMF decomposition products have been documented in Section 3; other examples are now collected.

While DMF adducts of transition metals, such as AgX(DMF) (X=BF_4, ClO_4)[3] and $PdX_2(DMF)_2$ (X=Cl, BF_4, ClO_4)[56] are stable at room temperature, heating of Cu^{II} and Ag^{I} salts in aqueous DMF led to their reduction to Cu^{I} species[53,57] and Ag nanoparticles,[58] respectively. The reduction of Au^{III} into Au nanoparticules with 4-aminothiophenol is also promoted by aqueous DMF.[59] It has been envisaged that DMF could react with water to produce formic acid,[60] which could reduce metal compounds.[37,61]

Reduction of $Pd(OAc)_2$ by DMF at 80 °C has been suspected, even in the absence of water. Under these conditions, the DMF decomposition products, i.e., carbon monoxide and dimethylamine, could be involved in the process.[62] Indeed, it has been reported that alkylamines containing α-C–H bonds reduce $PdCl_2L_2$ (L=PhCN, PPh_3, $OPPh_3$) into Pd^0 species,[63] but, according to a report from Alper and Grushin, traces of water are, in fact, required.[64] Kalck et al. have, however, observed that refluxing $PdCl_2$ in DMF for 10 min led to colloidal palladium suspensions, while, at 100 °C for 2 h, $PdCl_2(DMF)_2$ was isolated in 25% yield.[34]

To be efficient, the reduction of the transition metal has to be carried out under anaerobic conditions, since reoxidation can, in DMF, occur in the presence of oxygen, as observed for the $Pd^0 \rightarrow Pd^{II}$ reaction.[65]

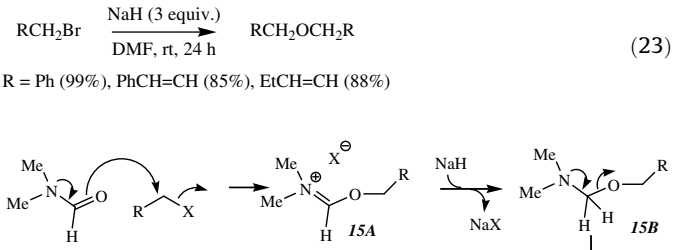
In the course of the study of Heck-type reactions using an inorganic base in DMF,[66] we have observed some debromation of aryl bromides. Such Pd-catalysed reduction, which depends upon the experimental conditions, also occurs from aryl iodides, but is inefficient from aryl chlorides. The formation of the deuterated arene in DMF-d_7 has demonstrated the role of the solvent, and has allowed the proposal of the mechanism shown in Scheme 14. Dimethylamine, in situ produced by base-mediated decomposition of DMF, reacts with the halogenopalladium complex **14A** to yield **14B**, which suffers a β-H elimination, leading to the hydridopalladium complex **14C**. Reductive elimination of Pd^0 from **14C** releases ArH.[67] Note that the DMF-mediated dehalogenation of aryl halides under Pd catalysis was envisaged, previously, by the teams of Heitz[68] and Fiaud[69] and, recently, by those of Maier[70] and Kim.[71,72] We suspect that the increase in the performance of Pd-catalysed reductions when they are carried out in DMF[73–75] could be due to the participation of the solvent as a complementary hydride source.

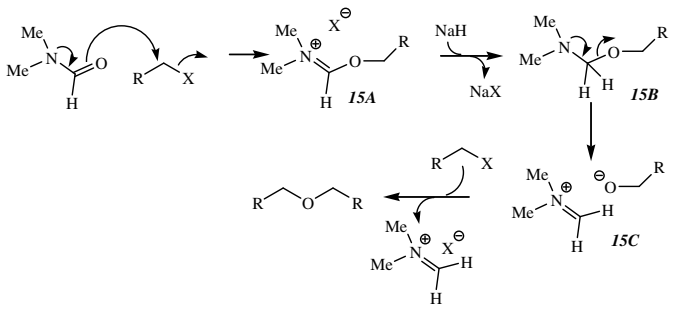


Scheme 14.

7. Source of oxygen atom

The treatment of allylic and benzylic bromides by sodium hydride in DMF affords the corresponding symmetrical ethers in high yields (Eq. 23).[76] The reaction occurs also from benzyl chloride, mesylate and tosylate, and (4-bromobutyl)benzene but with lower yields. The demonstration, using DMF-^{18}O, that the solvent provides the oxygen atom has led Jung et al. to propose[76] the mechanism depicted on Scheme 15. The addition of DMF to the substrate

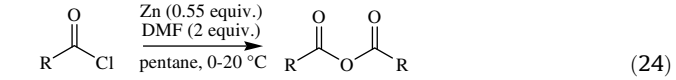


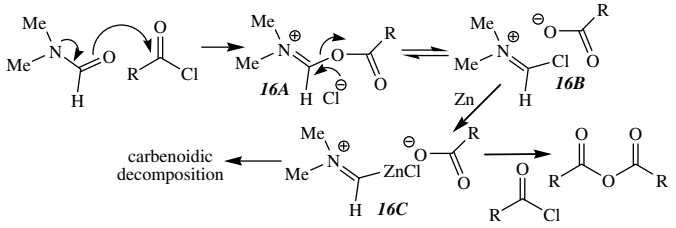


Scheme 15.

leads to the ammonium salt **15A** which is attacked by hydride to yield **15B** and then **15C**. The S_N2 reaction of the alkoxide anion of **15C** with the substrate affords the symmetric ether.

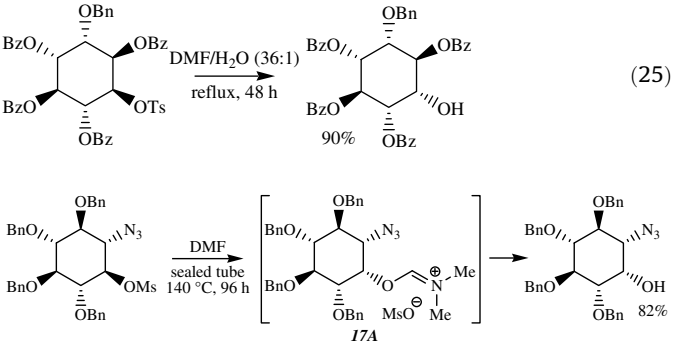
Symmetrical anhydrides have been obtained from acid chlorides, DMF and zinc dust (Eq. 24).[77] The suggested mechanism (Scheme 16) involves, as above, the addition of DMF to the substrate, affording the ammonium salt **16A** which is in equilibrium with **16B**. Reaction with Zn leads to **16C**. The anion of **16C** reacts with the substrate yielding the anhydride while the cation decomposes.





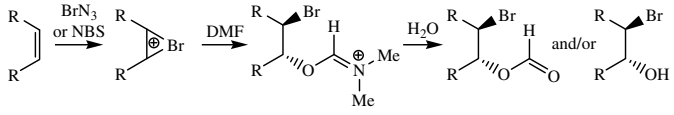
Scheme 16.

Heating of tosylates (Eq. 25)[78] or mesylates (Scheme 17)[79] in DMF for prolonged reaction times can afford alcohols with excellent stereocontrol. Such a reaction, that is not general (see Eq. 37 in Section 9), would occur via an S_N2 displacement by DMF, leading to an imidate ester salt **17A** as intermediate (Scheme 17).[79]



Scheme 17.

The bromonium ion obtained from the addition of *N*-bromosuccinimide or bromoazide to a C=C bond, reacts with DMF to yield the corresponding bromoformate and/or bromohydrin.[80,81] Following an experiment using DMF/^{18}O that has established the provenance of the oxygen atom of the C–O bond, the mechanism shown in Scheme 18 has been proposed.[81]

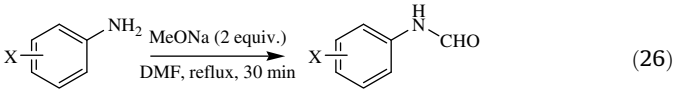


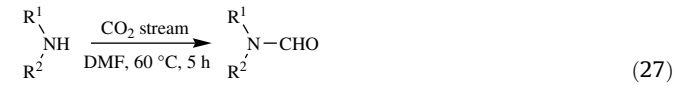
Scheme 18.

8. Source of formyl unit[‡]

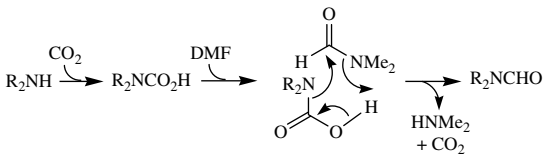
Various substrates have been formylated using Vilsmeier reagents but, as pointed out in the introduction section, these processes are out of the scope of the present review. Consequently, this section will summarise other formylation processes.

Amines are formylated using DMF as reagent with an efficiency depending upon their structure and on the experimental conditions. In 1959, Pettit and Thomas reported the sodium methoxide-mediated formylation of primary aryl amines in refluxing DMF (Eq. 26).[82] These conditions led to low yields of *N*-octylformamide from 1-aminooctane.[83] A mechanism similar to that depicted in Scheme 12, or the reaction of the substrate with carbon monoxide produced from the MeONa-mediated decomposition of DMF could be involved.[32] It is, however, known that catalysis is required for N-formylation with CO.[84] In contrast to the above method, the formylation of primary and secondary alkyl amines occurs easily under a stream of carbon dioxide, at 60 °C in DMF (Eq. 27), while aryl amines were not formylated.[85] Otsuji et al. have proposed[85] the mechanism depicted in Scheme 19: reaction of the amine with CO_2 produces the corresponding carbamic acid which reacts with DMF. Subsequently, Kraus reported the uncatalysed formylation of aliphatic amines (negligible reaction from aniline) via refluxing in DMF for prolonged periods (Eq. 28), while the addition of sulfuric acid enhanced the rate of the reaction (Eq. 29).[83] Takahashi et al., who have also noted the beneficial effect of sulfuric acid, have proposed a method based on the use, in DMF, of alumina, silicic acid and, especially, zirconium oxide, which allows the formylation in high yields of both aliphatic and aryl amines (Eq. 30).[86] Iwata and Kuzuhara have used 1.5 equiv, per NH_2 group, of 2,3-dihydro-1,4-phthalazinedione to promote the N-formylation of primary amines with DMF. These authors have suggested the formation of a ternary complex as the key transition state corresponding, however, to a mechanism requiring only catalytic amounts of the promoter (Scheme 20).[87]

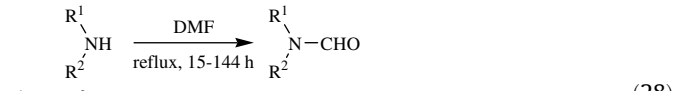




‡ See also Eq. 19.

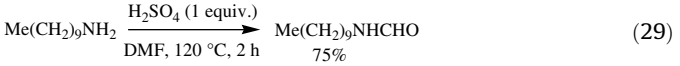


Scheme 19.

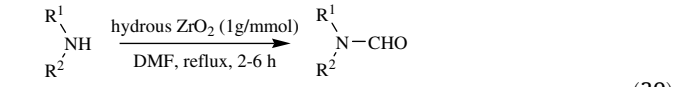


(28)

R^1 = H, R^2 = $Me(CH_2)_7$ (53 h, 91%), $Me(CH_2)_9$ (48 h, 83%), $Me(CH_2)_{11}$ (15 h, 98%), $Me(CH_2)_{17}$ (32 h, 88%), Bn (30 h, 90%), PhCHMe (144 h, 71%)
R^1-R^2 = $(CH_2)_5$ (90 h, 95%)

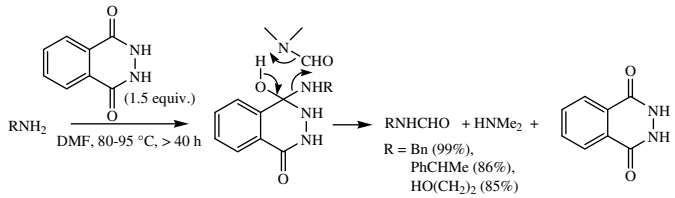


(29)



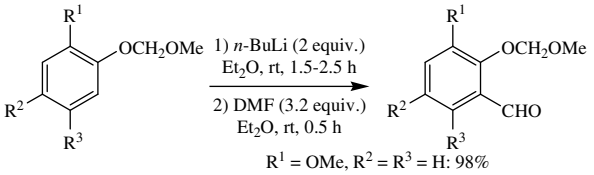
(30)

R^1 = H, R^2 = $Me(CH_2)_9$ (100%), Bn (99%), PhCHMe (100%)
R^1 = R^2 = *i*-Bu (96%), *n*-Bu (100%), cyclohexyl (100%)
R^1-R^2 = $(CH_2)_5$ (100%), $Me_2CH(CH_2)_3CHMe_2$ (69%), $(CH_2)_6$ (100%), (pyridin-3-yl)$CH(CH_2)_3$ (92%)



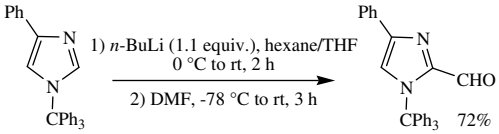
Scheme 20.

Organolithium compounds are formylated by DMF[88] (Eqs. 31,[89] 32[90] and 33[91]), with possible enantioselectivity induced by (−)-sparteine (Eq. 34).[92] In contrast to the mechanisms depicted in Schemes 15 and 16, the reaction occurs via the addition to DMF (Scheme 21), hydrolysis of the alcoholate thus formed affording the aldehyde.

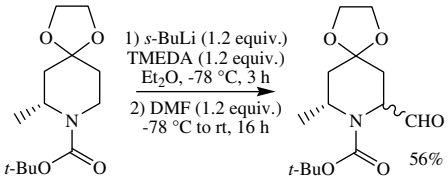


(31)

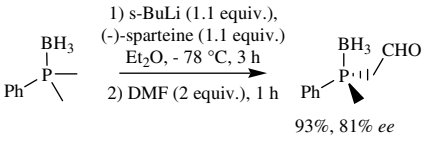
R^1 = OMe, R^2 = R^3 = H: 98%
R^1 = R^2 = H, R^3 = OMe: 90%
R^1 = H, R^2 = OMe, R^3 = H: 97%



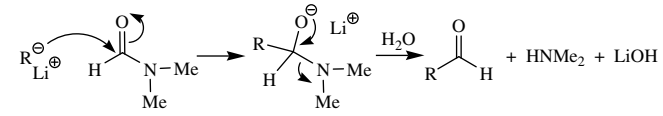
(32)



(33)

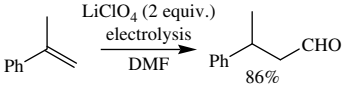


(34)

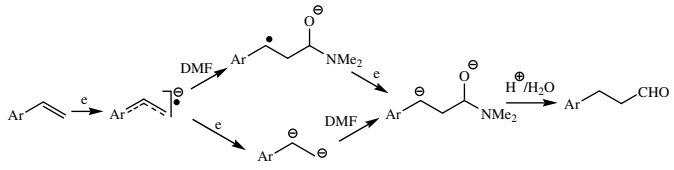


Scheme 21.

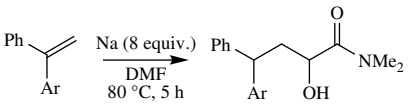
Aryl olefins are hydroformylated under electrochemical conditions in DMF (Eq. 35) via a reaction involving the addition of the radical anion or the dianion of the substrate to DMF (Scheme 22).[93] Hydroformylation of 1,1-diarylethenes followed by nucleophilic attack of the anion Me_2NCO^- formed by the action of sodium on DMF[94] has been one of the proposals to rationalise the formation of α-hydroxybutamides depicted in Eq. 36.[95]



(35)



Scheme 22.

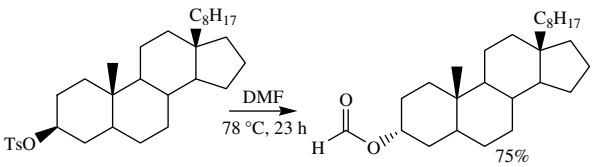


(36)

Ar = Ph (93%), 2-pyridyl (nearly 100%)

9. Source of formate unit[§]

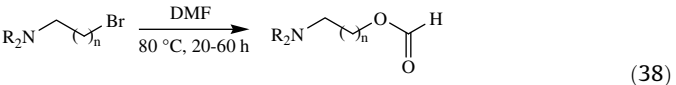
Heating 3β-cholestanyl tosylate at 78 °C in DMF yields 3α-cholestanyl formate (Eq. 37).[96] This contrasts with the displacement of tosylates depicted in Eq. 25, and is possibly due to the hydrolysis of the imidate ester salt formed as an intermediate from an S_N2 reaction with DMF (see intermediate of Scheme 17 with Ts instead of Ms).



(37)

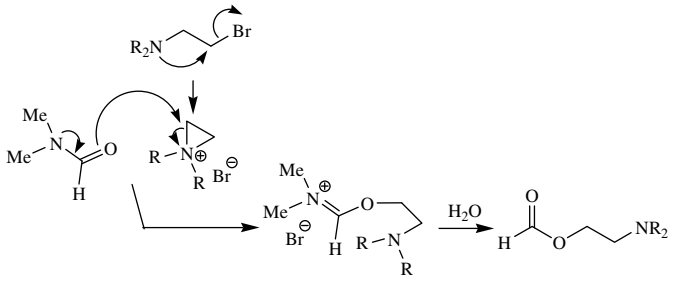
Heating 2-bromoethylamines and 3-bromopropylamines in DMF affords formate esters in good yields (Eq. 38).[97] The formation, under similar experimental conditions, of benzyl formate in low yield (7% in 20 h) from benzyl bromide has led Katerinopoulos et al. to propose[97] the participation of the nitrogen atom when bromoamines were the substrates (Scheme 23).

§ See also Scheme 18.



n = 1, R = CH_2CN (20 h, 66%), CH_2CO_2t-Bu (20 h, 76%), Bn (40 h, 97%)
n = 2, R = Bn (60 h, 80%)

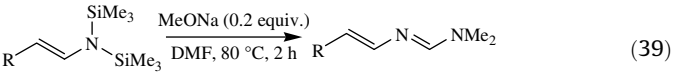
(38)



Scheme 23.

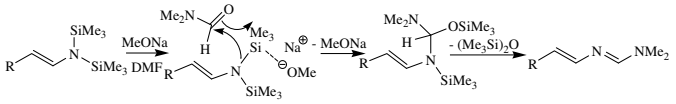
10. Source of Me_2NCH and CHOH units

Enamidines have been synthesised from *N*,*N*-bis(silyl) enamines and DMF under sodium methoxide catalysis (Eq. 39).[98] A possible role of the catalyst is to weaken a silicon-nitrogen bond through coordination at the silicon center (Scheme 24).[98]



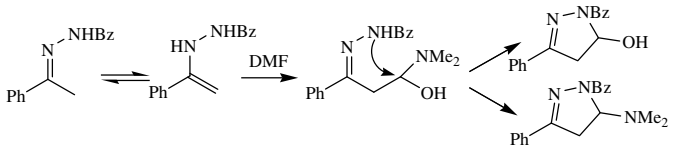
R = Me (82%), Me_3SiCH_2 (60%)

(39)



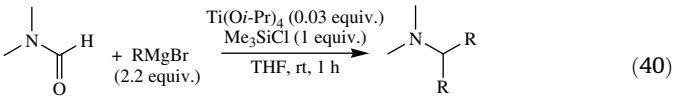
Scheme 24.

The synthesis of homoallylic amines from the addition of allylic trichlorosilanes to *N*-benzoylhydrazones (see Section 2, Scheme 8), can be accompanied by the formation of dihydropyrazoles due to the addition of the tautomeric isomer of the substrate, i.e., the corresponding enamine, to DMF (Scheme 25).[28]



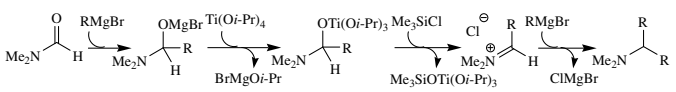
Scheme 25.

Dimethyl alkyl amines are obtained from the addition of Grignard reagents to DMF in the presence of $Ti(Oi\text{-}Pr)_4$ and Me_3SiCl (Eq. 40).[99] According to de Meijere et al.,[99] the mechanism of this process is not clear; one of the suggested possibilities is depicted in Scheme 26.



R = Ph (66%), *p*-MeC_6H_4 (40%), *p*-$MeOC_6H_4$ (80%)

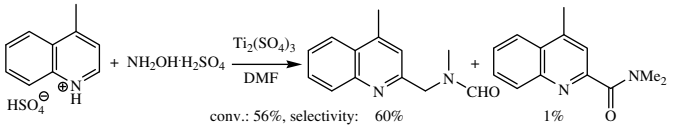
(40)



Scheme 26.

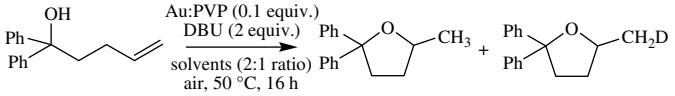
11. Source of radicals[¶]

In DMF, the redox system $[NH_3OH]^+/Ti^{III}$ induces the selective carbamoylation of protonated heteroaromatic bases by the $H_2NCO^{\bullet}$ radical (Eq. 41).[100]



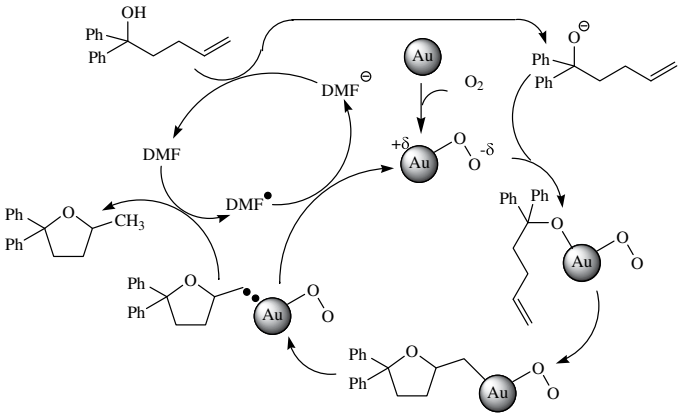
(41)

Sakurai et al. carried out the cycloisomerisation of a variety of γ-hydroxy alkenes, under an air atmosphere, using a gold nanocluster, denoted Au:PVP, as the catalyst, in a 2:1 H_2O/DMF mixture containing DBU (Eq. 42).[101,102] The participation of a hydrogen atom from DMF has been demonstrated using DMF-d_7 as the co-solvent (Eq. 42). According to the mechanism suggested by the authors (Scheme 27), this hydrogen is provided via a radical process.[101] We are not too confident in the proposed mechanism, because it does not take DBU into account. We suspect that the hydrogen atom could be from dimethylamine produced from the DBU-promoted decomposition of DMF. In fact, the large excess of DMF does not necessitate its regeneration, and DBU can promote the formation of the gold alkoxide.



solvents	conversion %	yield %	
H_2O/DMF:	100	87	-
D_2O/DMF:	97	80	0
H_2O/DMF-d_7:	68	0	63
D_2O/DMF-d_7:	50	0	42

(42)

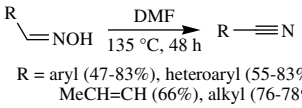


Scheme 27.

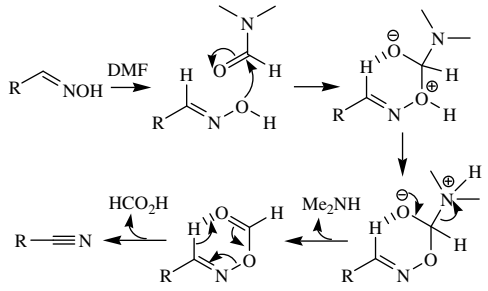
12. Dehydrating agent

The scope of the thermal dehydration of aldoximes in DMF, a reaction discovered by Liebscher and Hartmann in 1975,[103] has been recently examined by Varvounis et al. (Eq. 43), who have proposed the mechanism shown in Scheme 28.[104] According to these authors, DMF works 'three ways towards aldoximes, as a solvent, as a formylating agent and as a means of inducing thermal elimination of formic acid to give the nitrile'.[104]

[¶] See also Eq. 20 and corresponding text.



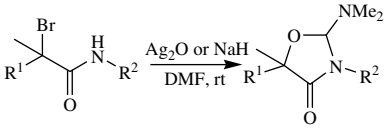
(43)



Scheme 28.

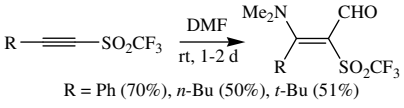
13. Cycloadditions

In the presence of NaH,[105,106] Ag_2O,[105] or under electrochemical reduction conditions,[107] α-bromoamides react with the carbonyl group of DMF to afford 2-(dimethylamino)oxazolidin-4-ones (Eq. 44). The 2-bromoamide anion would be involved as an intermediate.[105,107]

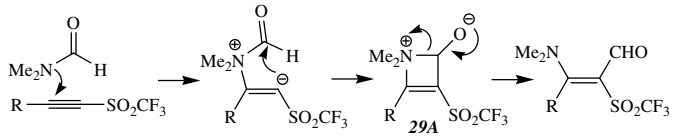


(44)

The reaction of alkynyl trifluoromethyl sulfones with DMF that yields the adducts shown in Eq. 45 would occur via the four-membered heterocycle **29A** (Scheme 29).[108]



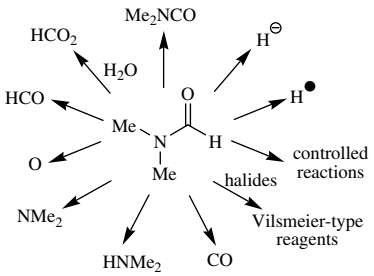
(45)



Scheme 29.

14. Conclusions

The present review shows that, besides being an effective polar solvent, DMF is a multipurpose reagent participating, thanks to its structure, in various reactions. It is necessary to point out that some of these also occur using other amides, and to remember the use, undisclosed in this review, of DMF to form Vilsmeier reagents. The different roles of DMF in organic synthesis are summarised in Scheme 30.



Scheme 30.

15. Addendum

Sanz et al. have recently suggested the formation of an ammonium formate derivative from a DMF solution containing a palladium catalyst and diethylamine; this species would be involved in the reduction of a C≡C bond and a NO_2 unit.[109]

References and notes

1. Gutmann, V. *Coordination Chemistry in Non-aqueous Solutions*; Springer: Wien, 1968; pp 152–154; Hosokawa, T.; Nomura, T.; Murahashi, S.-I. *J. Organomet. Chem.* **1998**, *551*, 387–389; Jutand, A. *Eur. J. Inorg. Chem.* **2003**, 2017–2040; Aresta, M.; Pastore, C.; Giannoccaro, P.; Kovács, G.; Dibenedetto, A.; Pápai, I. *Chem.—Eur. J.* **2007**, *13*, 9028–9034; Jutand, A. *Chem. Rev.* **2008**, *108*, 2300–2347; Álvarez, R.; Pérez, M.; Faza, O. N.; de Lera, A. R. *Organometallics* **2008**, *27*, 3378–3389.
2. Amatore, C.; Jutand, A.; Meyer, G.; Carelli, I.; Chiarotto, I. *Eur. J. Inorg. Chem.* **2000**, 1855–1859.
3. Kuhn, S. J.; McIntyre, J. S. *Can. J. Chem.* **1965**, *43*, 995–998.
4. Gore, E. S.; Blears, D. J.; Danyluk, S. S. *Can. J. Chem.* **1965**, *43*, 2135–2140.
5. Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic Chemistry*; Oxford University Press: Oxford, 2001; p 1158.
6. Jutz, C. In *Advances in Organic Chemistry*; Taylor, E. C., Ed.; Wiley, J: New York, NY, 1976; Vol. 9, pp 225–342; Meth-Cohn, O.; Stanforth, S. P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: London, 1991; Vol. 2, pp 777–794; Marson, C. M. *Tetrahedron* **1992**, *48*, 3659–3726; Jones, G.; Stanforth, S. P. In *Organic Reactions*; Paquette, L. A., Ed.; Wiley: New York, NY, 1997; Vol. 49, pp 1–330; Gilles, P. R.; Marson, C. M. In *Handbook of Reagents for Organic Synthesis; Reagents, Auxiliaries, and Catalysts for C–C Bond Formation*; Coates, R. M., Denmark, S. E., Eds.; Wiley: Chichester, UK, 1999; pp 309–312; Comins, D. L.; Joseph, S. P. In *Handbook of Reagents for Organic Synthesis; Reagents, Auxiliaries, and Catalysts for C–C Bond Formation*; Coates, R. M., Denmark, S. E., Eds.; Wiley: Chichester, UK, 1999; pp 312–315; Jones, G.; Stanforth, S. P. In *Organic Reactions*; Overman, L. O., Ed.; Wiley: New York, NY, 2000; Vol. 56; pp 355–659; Brahma, S.; Ray, J. K. *Tetrahedron* **2008**, *64*, 2883–2896.
7. For the Wacker reaction, see: Tsuji, J. *Synthesis* **1984**, 369–384; For recent examples, see: Kiyooka, S.; Matsumoto, S.; Kojima, M.; Sakonaka, K.; Maeda, H. *Tetrahedron Lett.* **2008**, *49*, 1589–1592; Majumdar, K. C.; Chattopadhyay, B.; Nath, S. *Tetrahedron Lett.* **2008**, *49*, 1609–1612; Zhong, W.; Liu, Z.; Yu, C.; Su, W. *Synlett* **2008**, 2888–2892; Huang, H.; Liu, H.; Jiang, H.; Chen, K. *J. Org. Chem.* **2008**, *73*, 6037–6040; Wu, M.; Mao, J.; Guo, J.; Ji, S. *Eur. J. Org. Chem.* **2008**, 4050–4054; Chaumontet, M.; Piccardi, R.; Audic, N.; Hitce, J.; Peglion, J.-L.; Clot, E.; Baudoin, O. *J. Am. Chem. Soc.* **2008**, *130*, 15157–15166; Tu, S.-J.; Yan, S.; Cao, X.-D.; Wu, S.-S.; Zhang, X.-H.; Hao, W.-J.; Han, Z.-G.; Shi, F. *J. Organomet. Chem.* **2008**, *694*, 91–96; Jana, R.; Chatterjee, I.; Samanta, S.; Ray, J. K. *Org. Lett.* **2008**, *10*, 4795–4797; Majumdar, K. C.; Chattopadhyay, B.; Sinha, B. *Synthesis* **2008**, 3857–3863; Luo, H.-Q.; Loh, T.-P. *Tetrahedron Lett.* **2009**, *50*, 1554–1556; Majumdar, K. C.; Sinha, B.; Maji, P. K.; Chattopadhyay, S. K. *Tetrahedron* **2009**, *65*, 2751–2756; Kobayashi, K.; Kondo, Y. *Org. Lett.* **2009**, *11*, 2035–2037.
8. Hagiwara, H.; Iijima, D.; Awen, B. Z. S.; Hoshi, T.; Suzuki, T. *Synlett* **2008**, 1520–1522.
9. Alcaide, B.; Almendros, P.; Martínez del Campo, T.; Carrascoa, R. *Chem. Asian J.* **2008**, *3*, 1140–1145.
10. Zawisza, A. M.; Bouquillon, S.; Muzart, J. *Eur. J. Org. Chem.* **2007**, 3901–3904.
11. Evans, L. A.; Fey, N.; Harvey, J. N.; Hose, D.; Lloyd-Jones, G. C.; Murray, P.; Orpen, A. G.; Osborne, R.; Owen-Smith, G. J. J.; Purdie, M. *J. Am. Chem. Soc.* **2008**, *130*, 14471–14473.
12. For a recent report on the solvent-depending shape of reaction profiles, see: van Bochove, M. A.; Bikelhaupt, F. M. *Eur. J. Org. Chem.* **2008**, 649–654.
13. Parker, A. J. *Chem. Rev.* **1969**, *69*, 1–32.
14. For a recent study, see: Amatore, C.; Catellani, M.; Deladda, S.; Jutand, A.; Motti, E. *Organometallics* **2008**, *27*, 4549–4554.
15. Amatore, C.; Jutand, A.; Meyer, G.; Mottier, L. *Chem.—Eur. J.* **1999**, *5*, 466–473.
16. Bouquillon, S.; Muzart, J. *Eur. J. Org. Chem.* **2001**, 3301–3305.
17. Amatore, C.; Jutand, A.; Mottier, L. *Eur. J. Inorg. Chem.* **1999**, 1081–1085.
18. Narahashi, H.; Shimizu, I.; Yamamoto, A. *J. Organomet. Chem.* **2008**, *693*, 283–296.

19. See also: Ludwig, M.; Strömberg, S.; Svensson, M.; Åkermark, B. *Organometallics* **1999**, *18*, 970–975.
20. Kovala-Demertzi, D.; Kourkoumelis, N.; West, D. X.; Valdés-Martínez, J.; Hernández-Ortega, S. *Eur. J. Inorg. Chem.* **1998**, 861–863.
21. Sugawara, Y.; Yamada, W.; Yoshida, S.; Ikeno, T.; Yamada, T. *J. Am. Chem. Soc.* **2007**, *129*, 12902–12903.
22. De Kimpe, N.; De Buyck, L.; Verhe, R.; Wychuyse, F.; Schamp, N. *Synth. Commun.* **1979**, *9*, 575–592.
23. Jiang, J.-L.; Xiu, Z.; Hua, R. *Synth. Commun.* **2008**, *38*, 232–238.
24. Satgé, C.; Le Bras, J.; Hénin, F.; Muzart, J. *Tetrahedron* **2005**, *61*, 8405–8409.
25. Nishida, Y.; Shingu, Y.; Dohi, H.; Kobayashi, K. *Org. Lett.* **2003**, *5*, 2377–2380.
26. Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, *34*, 3453–3456; Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *5967*, 6620–6628.
27. Kobayashi, S.; Hirabayashi, R. *J. Am. Chem. Soc.* **1999**, *121*, 6942–6943.
28. Ogawa, C.; Sugiura, M.; Kobayashi, S. *J. Org. Chem.* **2002**, *67*, 5359–5364.
29. Hirabayashi, R.; Ogawa, C.; Sugiura, M.; Kobayashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 9493–9499.
30. Ogawa, C.; Sugiura, M.; Kobayashi, S. *Synlett* **2003**, 1749–1751.
31. Wu, P.; Sun, J. *Synth. Commun.* **2008**, *38*, 1003–1010.
32. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1966; p 143.
33. Rusina, A.; Vlček, A. A. *Nature* **1965**, *206*, 295–296.
34. Serp, P.; Hernandez, M.; Richard, B.; Kalck, P. *Eur. J. Inorg. Chem.* **2001**, 2327–2336. This report contains an informative short survey of the literature on the reactions of DMF with metal complexes.
35. Serp, P.; Hernandez, M.; Kalck, P. *C. R. Acad. Sci. Paris, Série IIc: Chimie* **1999**, *2*, 267–272.
36. Coalter, J. N., III; Huffman, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569–3578.
37. Tsuji, J.; Mandai, T. *Synthesis* **1996**, 1–24.
38. Wu, X.; Mahalingam, A. K.; Wan, Y.; Alterman, M. *Tetrahedron Lett.* **2004**, *45*, 4635–4638.
39. Coppinger, G. M. *J. Am. Chem. Soc.* **1954**, *76*, 1372–1373.
40. Balogh-Hergovich, É.; Speier, G. *J. Chem. Soc., Chem. Commun.* **1991**, 551–552; Balogh-Hergovich, É.; Kaizer, J.; Speier, G. *J. Mol. Catal. A: Chem.* **2000**, *159*, 215–224; Balogh-Hergovich, É.; Kaizer, J.; Speier, G.; Huttner, G.; Jacobi, A. *Inorg. Chem.* **2000**, *39*, 4224–4229.
41. March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill Book: New York, NY, 1977; p 383.
42. Kadish, K. M.; Han, B. C.; Franzen, M. M.; Araullo-McAdams, C. *J. Am. Chem. Soc.* **1990**, *112*, 8364–8368.
43. Agarwal, A.; Chauhan, P. M. S. *Synth. Commun.* **2004**, *34*, 2925–2930.
44. Heindel, N. D.; Kennewell, P. D. *Chem. Commun.* **1969**, 38; Watanabe, T.; Tanaka, Y.; Sekiya, K.; Akita, Y.; Ohta, A. *Synthesis* **1980**, 39–41.
45. D'Amico, J. J.; Webster, S. T.; Campbell, R. H.; Twine, C. E. *J. Org. Chem.* **1965**, *30*, 3618–3625.
46. Sharma, A.; Mehta, V. P.; Van der Eycken, E. *Tetrahedron* **2008**, *64*, 2605–2610.
47. Cho, Y. H.; Park, J. C. *Tetrahedron Lett.* **1997**, *38*, 8331–8334.
48. Nasipuri, D.; Bhattacharyya, A.; Hazra, B. G. *J. Chem. Soc., Chem. Commun.* **1971**, 660–661.
49. Powers, J. C.; Seidner, R.; Parsons, T. G. *Tetrahedron Lett.* **1965**, 1713–1716.
50. Paul, S.; Schmidt, R. R. *Synlett* **2002**, 1107–1108.
51. Filali, E.; Lloyd-Jones, G.; Sale, D. A. *Synlett* **2009**, 205–208.
52. Toffano, M.; Legros, J.-Y.; Fiaud, J.-C. *Tetrahedron Lett.* **1997**, *38*, 77–80.
53. Malkhasian, A. Y. S.; Finch, M. E.; Nikolovski, B.; Menon, A.; Kucera, B. E.; Chavez, F. A. *Inorg. Chem.* **2007**, *46*, 2950–2952.
54. For the accurate structure of the Cu catalyst, see: Warden, A. C.; Spiccia, L.; Hearn, M. T. W.; Boas, J. F.; Pilbrow, J. R. *J. Chem. Soc., Dalton Trans.* **2005**, 1804–1813.
55. Wan, Y.; Alterman, M.; Larhed, M.; Hallberg, A. *J. Org. Chem.* **2002**, *67*, 6232–6235.
56. Wayland, B. B.; Schramm, R. F. *Inorg. Chem.* **1969**, *8*, 971–976.
57. Teo, J. J.; Chang, Y.; Zeng, H. C. *Langmuir* **2006**, *22*, 7369–7377.
58. Pastoriza-Santos, I.; Liz-Marzán, L. M. *Nano Lett.* **2002**, *2*, 903–905.
59. Sharma, J.; Mahima, S.; Kakade, B. A.; Pasricha, R.; Mandale, A. B.; Vijayamohanan, K. *J. Phys. Chem. B* **2004**, *108*, 13280–13286.
60. Pletnev, A. A.; Tian, Q.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 9276–9287.
61. Cacchi, S.; Felici, M.; Pietroni, B. *Tetrahedron Lett.* **1984**, *25*, 3137–3140.
62. Penalva, V.; Lavenot, L.; Gozzi, C.; Lemaire, M. *Appl. Catal. A: Gen.* **1999**, *182*, 399–405.
63. McCrindle, R.; Ferguson, G.; Arsenault, G. J.; McAlees, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 571–572; McCrindle, R.; Ferguson, G.; Arsenault, G. J.; McAlees, A. J.; Stephenson, D. K. *J. Chem. Res., Synop.* **1984**, 360–361; *J. Chem. Res., Miniprint* **1984**, 3301–3344; Trzeciak, A. M.; Ciunik, Z.; Ziółkowski, J. J. *Organometallics* **2002**, *21*, 132–137.
64. Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890–1901.
65. El Kaïm, L.; Gamez-Montaño, R.; Grimaud, L.; Ibarra-Rivera, T. *Chem. Commun.* **2008**, 1350–1352.
66. Zawisza, A. M.; Ganchegui, B.; González, I.; Bouquillon, S.; Roglans, A.; Hénin, F.; Muzart, J. *J. Mol. Catal. A: Chem.* **2008**, *283*, 140–145.
67. Zawisza, A. M.; Muzart, J. *Tetrahedron Lett.* **2007**, *48*, 6738–6742.
68. Brenda, M.; Knebelkamp, A.; Greiner, A.; Heitz, W. *Synlett* **1991**, 809–810.
69. Legros, J.-Y.; Primault, G.; Toffano, M.; Rivière, M.-A.; Fiaud, J.-C. *Org. Lett.* **2000**, *4*, 433–436.
70. Satyanarayana, G.; Maier, M. E. *J. Org. Chem.* **2008**, *73*, 5410–5415.
71. Kim, H. S.; Gowrisankar, S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 3858–3861; Kim, H. S.; Lee, H. S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2009**, *50*, 3154–3157.
72. See also Alterman's report.
73. Zask, A.; Helquist, P. *J. Org. Chem.* **1978**, *43*, 1619–1620.
74. Lassová, L.; Lee, H. K.; Hor, T. S. A. *J. Mol. Catal. A: Chem.* **1999**, *144*, 397–403.
75. The Zask/Helquist procedure[73] has been recently used for the dehalogenation of a vinyl bromide: Taniguchi, N. *Synlett* **2008**, 849–852.
76. Jin, C. H.; Lee, H. Y.; Lee, S. H.; Kim, I. S.; Jung, Y. H. *Synlett* **2007**, 2695–2698.
77. Serieys, A.; Botuha, C.; Chemla, F.; Ferreira, F.; Pérez-Luna, A. *Tetrahedron Lett.* **2008**, *49*, 5322–5323.
78. Angyal, S. J.; Odier, L. *Carbohydr. Res.* **1980**, *80*, 203–206.
79. Serrano, P.; Llebaria, A.; Delgado, A. *J. Org. Chem.* **2005**, *70*, 7829–7840.
80. Boerwinkle, F.; Hassner, A. *Tetrahedron Lett.* **1968**, 3921–3924.
81. Dalton, D. R.; Smith, J. R., Jr.; Jones, D. G. *Tetrahedron* **1970**, *26*, 575–581.
82. Pettit, G. R.; Thomas, E. G. *J. Org. Chem.* **1959**, *24*, 895–896.
83. Kraus, M. A. *Synthesis* **1973**, 361–362.
84. March, J. *Advanced Organic Chemistry*, 4th ed.; McGraw-Hill Book: New York, NY, 1992; p 640.
85. Otsuji, Y.; Matsumura, N.; Imoto, E. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1485.
86. Takahashi, K.; Shibagaki, M.; Matsushita, H. *Agric. Biol. Chem.* **1988**, *52*, 853–854.
87. Iwata, M.; Kuzuhara, H. *Chem. Lett.* **1989**, *11*, 2029–2030.
88. Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1077–1078; Khanapure, S. P.; Manna, S.; Rokach, J.; Murphy, R. C.; Wheelan, P.; Powell, W. S. *J. Org. Chem.* **1995**, *60*, 1806–1813; Groth, U.; Köttgen, P.; Langenbach, P.; Lindenmaier, A.; Schütz, T.; Wiegand, M. *Synlett* **2008**, 1301–1304.
89. Narasimhan, N. S.; Mali, R. S.; Barve, M. V. *Synthesis* **1979**, 906–909.
90. Kumar, S.; Jaller, D.; Patel, B.; LaLonde, J. M.; DuHadaway, J. B.; Malachowski, W. P.; Prendergast, G. C.; Muller, A. J. *J. Med. Chem.* **2008**, *51*, 4968–4977.
91. Pizzuti, M. B.; Minnaard, A. J.; Feringa, B. L. *Org. Biomol. Chem.* **2008**, *6*, 3464–3466.
92. Johansson, M. J.; Andersson, K. H. O.; Kann, N. *J. Org. Chem.* **2008**, *73*, 4458–4463.
93. Engels, R.; Schäfer, H. J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 460.
94. Young, C. A.; Dewald, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 2884–2888.
95. Botteghi, C.; Gotta, S.; Marchetti, M.; Melloni, G. *Tetrahedron Lett.* **1992**, *33*, 5601–5602.
96. Chang, F. C.; Blickenstaff, R. T. *J. Am. Chem. Soc.* **1958**, *80*, 2906.
97. Dakanali, M.; Tsikalas, G. K.; Krautscheid, H.; Katerinopoulos, H. E. *Tetrahedron Lett.* **2008**, *49*, 1648–1651.
98. Corriu, R. J. P.; Moreau, J. J. E.; Pataud-Sat, M. *J. Org. Chem.* **1990**, *55*, 2878–2884.
99. Tomashenko, O.; Sokolov, V.; Tomashevskiy, A.; Buchholz, H. A.; Welz-Biermann, U.; Chaplinski, V.; de Meijere, A. *Eur. J. Org. Chem.* **2008**, 5107–5111.
100. Minisci, F.; Citterio, A.; Vismara, E.; Giordano, C. *Tetrahedron* **1985**, *41*, 4157–4170.
101. Kamiya, I.; Tsunoyama, H.; Tsukuda, T.; Sakurai, H. *Chem. Lett.* **2007**, *36*, 646–647.
102. For a review on the Au-catalysed reactions of hydroxyalkenes, see: Muzart, J. *Tetrahedron* **2008**, *64*, 5815–5849.
103. Liebscher, J.; Hartmann, H. *Zeitschrift für Chemie* **1975**, *15*, 302.
104. Supsana, P.; Liaskopoulos, T.; Tsoungas, P. G.; Varvounis, G. *Synlett* **2007**, 2671–2674.
105. D'Angeli, F.; Cavicchioni, G.; Catelani, G.; Marchetti, P.; Maran, F. *Gazz. Chim. Ital.* **1989**, *119*, 471–474.
106. Scrimain, P.; D'Angeli, F.; Veronese, A. C.; Baiono, V. *Tetrahedron Lett.* **1983**, *24*, 4473–4476.
107. Maran, F.; Vianello, E.; Cavicchioni, G.; D'Angeli, F. *J. Chem. Soc., Chem. Commun.* **1985**, 660–661; Maran, F.; Vianello, E.; D'Angeli, F.; Cavicchioni, G.; Vecchiati, G. *J. Chem. Soc., Perkin Trans. 2* **1987**, 33–38.
108. Hanack, M.; Wilhelm, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1057–1059.
109. Sanz, R.; Guilarte, V.; Pérez, A. *Tetrahedron Lett.* **2009**, *50*, 4423–4426.

Biographical sketch

Jacques Muzart was born in 1946, in Vienne la Ville, a small village in the Argonne area, 200 km east of Paris. He studied chemistry at the Université de Champagne-Ardenne and received his degrees (Doctorat de 3ème cycle—1972, Doctorat d'Etat—1976) for his work with Jean-Pierre Pète on photochemical rearrangements of α,β-epoxyketones and β-diketones. He was appointed at the Centre National de la Recherche Scientifique (CNRS) in 1971 as Stagiaire de Recherche and spent 15 months (1977–1978) as a postdoctoral fellow of National Science Foundation working with Elias J. Corey at Harvard University on natural product synthesis. On his return to Reims, he mainly studied the photoreactivity of η^3-allylpalladium complexes and anionic activation by supported reagents. In 1988, he was promoted to Directeur de Recherche CNRS. His research interests concentrate on transition metal-catalysis with particular emphasis on oxidations, C–H activation, asymmetric reactions and mechanisms. He is also involved in the valorisation of agricultural by-products and in the use of water and molten salts as solvents for Organic Synthesis.