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Molybdenum-mediated imido-transfer reaction of *N*-sulfinylamines with dimethylformamide

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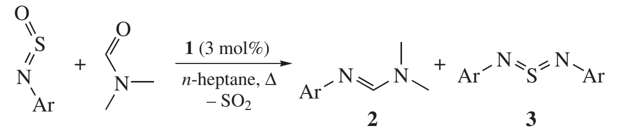
Dimethylformamide undergoes molybdenum-mediated metathetical imido-deoxygenation with *ortho*-substituted by donor atoms *N*-sulfinylanilines affording formamidines; *N*-sulfinylamines undergo molybdenum-mediated condensation into sulfurdiimines.

The metathesis of multiple carbon–carbon bonds is a powerful tool of fine organic synthesis.[1] Examples of transition-metal-mediated metathesis of carbon–heteroatom or heteroatom–heteroatom double bonds (heterometathesis) are still rare. In particular, metathesis of azomethines,[2] carbodiimides[3] and diphosphenes,[4] metathetical imido-deoxygenation of aldehydes with isocyanates[5] and *N*-sulfinylamines[6] affording imines, condensation of isocyanates into carbodiimides[7] have been reported. Among these processes, imido-transfer reactions are of interest because derivatives including an imino (imido) moiety are important organic compounds.

N-Sulfinylamines R–NSO undergo heterometathesis with aldehydes, ketones and ketoacid esters to give imines; however, the scope of reactive substrates is limited by only polyfluorinated compounds.[8] Recently, we have considerably extended the range of both *N*-sulfinylamines and aldehydes[6] by using vanadium and molybdenum oxochlorides or imidomolybdenum aroxides as catalysts in this reaction. Here, we report that carboxylic acid amides such as dimethylformamide (DMF) can also undergo metathetical imido-deoxygenation reaction with *N*-sulfinylamines mediated by molybdenum diimido dialkyl complex $(MesN)_2Mo(CH_2CMe_2Ph)_2$ (Mes = 2,4,6-$Me_3C_6H_2$) **1**.[†]

Table 1 Reaction of *N*-sulfinylamines ArNSO with DMF.



Entry	Ar	t/h	Yield of formamidine (%)		Yield of sulfurdiimine (%)	
1	2,4,6-$Cl_3C_6H_2$	5	**2a**	71^a (53^b)	**3a**	9
2	2-$CF_3C_6H_4$	5	**2b**	78 (73)	**3b**	9
3	2-FC_6H_4	20	**2c**	44	**3c**	43
4	2-$MeOC_6H_4$	20	**2d**	53	**3d**	25
5	4-$MeOC_6H_4$	no reaction				
6	2,4,6-$Me_3C_6H_2$	no reaction				

[a]Spectroscopically estimated. [b]Isolated.

The reaction of *N*-sulfinylamines with DMF occurs in the presence of imide **1** (3 mol%) in boiling *n*-heptane with SO_2 evolution affording formamidines **2a–d** in good to moderate yields (Table 1).[‡] The reaction is also catalysed by other molybdenum diimido dialkyl complexes, in particular, $(MesN)_2MoR_2$ (R = = CH_2SiMe_3, CH_2CMe_3), whereas no reaction was observed in the absence of catalyst. Interestingly, only *N*-sulfinylanilines bearing *o*-substituents with donor atoms (Table 1, entries 1–4) react with DMF but *o*-alkylated or *o*-unsubstituted compounds, for example, *N*-sulfinylmesitylamine and 4-methoxy-*N*-sulfinylaniline (Table 1, entries 5 and 6), are nonreactive. Apart from formamidines, sulfurdiimines **3a–d** formed as by-products in all cases (Table 1). This fact points out that the alternative oxo–imido exchange process occurs, in which *N*-sulfinylamines react simultaneously as both imidating agents and oxo-containing components. Indeed, under the same conditions in the absence of DMF, the condensation of *N*-sulfinylamines proceeds and results in sulfurdiimines (Table 2).[§] As mentioned above, only *o*-substituted by donor atoms *N*-sulfinylanilines are reactive.

[†] All manipulations were carried out under an argon atmosphere using standard Schlenk line technique. The ^1H and ^{13}C NMR spectra of **1** were recorded on a Bruker Avance-400 spectrometer (400.13 and 100.61 MHz, respectively) in C_6D_6. The ^1H and ^{19}F NMR spectra of **2a–d** and **3a–d** were recorded on a Bruker Avance 300 spectrometer (300.13 and 282.4 MHz, respectively) in $CDCl_3$. The residual solvent ^1H or ^{13}C resonances were used as internal references. The ^{19}F NMR spectra were referenced externally to TFA. Infrared spectra were measured on a Specord M80 spectrophotometer ($CHCl_3$). Mass spectra were measured on a Finnigan POLARIS Q (EI at 70 eV).

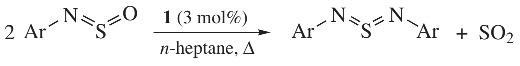
Preparation of $(MesN)_2Mo(CH_2CMe_2Ph)_2$ **1**. A solution of neophyl magnesium chloride in Et_2O (1.76 mol dm^{-3}, 3.3 ml, 5.8 mmol) was added dropwise to a stirred suspension of $(MesN)_2MoCl_2(dme)$ (1.51 g, 2.9 mmol) in Et_2O (120 ml) at –78 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 12 h. The resulting orange-red solution was filtered, concentrated in a vacuum to ~50 ml and cooled to –24 °C to afford analytically pure product as a yellow crystalline solid, which was filtered off and dried in a vacuum. The yield was 1.51 g (83%). ^1H NMR, δ: 7.43 (d, 4H, H_{Ph}, J 7.56 Hz), 7.21–7.17 (m, 4H, H_{Ph}), 7.08 (t, 2H, H_{Ph}, J 7.33 Hz), 6.68 (s, 4H, H_{Mes}), 2.17 (s, 12H, *o*-Me), 2.08 (s, 6H, *p*-Me), 1.76 (s, 4H, CH_2) 1.47 (s, 12H, Me). $^{13}C\{^1H\}$ NMR, δ: 154.61, 150.77, 134.12, 132.15, 128.66, 128.59, 126.67, 126.20, 76.44, 39.66, 32.30, 21.05, 18.83. Found (%): C, 72.42; H, 7.77; N, 4.45. Calc. for $C_{38}H_{48}MoN_2$ (%): C, 72.59; H, 7.69; N, 4.46.

[‡] *Reaction of* N*-sulfinylamines with DMF: general procedure*. A 100 ml Schlenk flask was charged with *N*-sulfinylamine (3 mmol), DMF (0.22 g, 3 mmol), $(MesN)_2Mo(CH_2CMe_2Ph)_2$ (0.06 g, 0.09 mmol, 3 mol%) as a catalyst and *n*-heptane (25–30 ml). The reaction mixture was stirred under reflux for 5 h for **2a**,**b** and 20 h for **2c**,**d**. The solution was filtered through a Celite® pad, the solvent was removed at a reduced pressure, and the residue was crystallised from concentrated solution in *n*-heptane at 5 °C (compound **2a**) or fractionated in a vacuum (compound **2b**).

N,N*-Dimethyl-*N'*-(2,4,6-trichlorophenyl)formamidine* **2a**: yield 0.4 g (53%); mp 69–71 °C (lit.,[10] 70–71 °C). ^1H NMR, δ: 7.35 (s, CH, 1H), 7.26 (s, 2H, H_{Ar}), 3.05 (d, 6H, NMe_2). IR (ν/cm^{-1}): 1640 (C=N). MS, m/z (%): 250 $[M]^+$ (28), 215 (100), 208 (18), 174 (27).

The spectral data of formamidines **2b–d** are given in the Online Supplementary Materials.

Table 2 Condensation of *N*-sulfinylamines ArNSO into sulfurdiimines.



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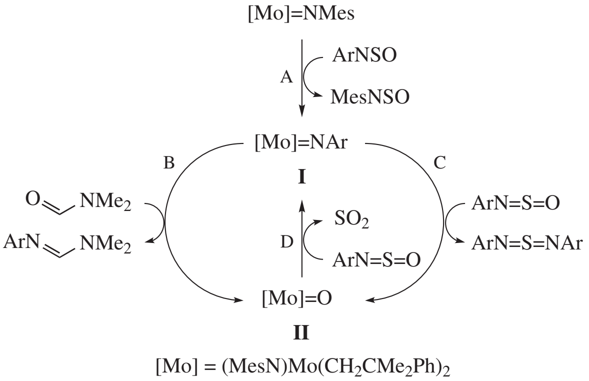
Entry	Ar	*t*/h	Yield of sulfurdiimine (%)	
1	2,4,6-$Cl_3C_6H_2$	5	**3a**	72[a] (62[b])
2	2-$CF_3C_6H_4$	7	**3b**	76 (52)
3	2-FC_6H_4	7	**3c**	65 (55)
4	2-$MeOC_6H_4$	7	**3d**	35
5	4-$MeOC_6H_4$	no reaction		
6	2,4,6-$Me_3C_6H_2$	no reaction		

[a] Spectroscopically estimated. [b] Isolated.

The proposed scheme of the imido-transfer reaction of *N*-sulfinylamines with DMF[¶] (Scheme 1) includes the initial step of transimidation of starting complex **1** with *N*-sulfinylamine (step A) affording respective arylimide **I** and *N*-sulfinylmesitylamine.[††] Further oxo-deimidation of complex **I** can proceed along two competitive routes under the action of either DMF (route B) or *N*-sulfinylamine (route C) to lead to oxide **II** and liberate formamidine or sulfurdiimine, respectively. The well-documented[9] imido-deoxygenation of **II** with *N*-sulfinylamine (step D) regenerates complex **I**.



Scheme 1

Thus, we have shown for the first time by the example of dimethylformamide that carboxylic acid amides undergo metathetical imido-deoxygenation with *N*-sulfinylamines under mediation of molybdenum diimido dialkyl complexes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2009.05.019.

References

1 *Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, 2003.

2 (*a*) G. K. Cantrell and T. Y. Meyer, *Chem. Commun.*, 1997, 1551; (*b*) G. K. Cantrell and T. Y. Meyer, *J. Am. Chem. Soc.*, 1998, **120**, 8035; (*c*) R. L. Zuckerman, S. W. Krska and R. G. Bergman, *J. Am. Chem. Soc.*, 2000, **122**, 751; (*d*) J.-W. Bruno and X. J. Li, *Organometallics*, 2000, **19**, 4672.

3 (*a*) K. Weiss and P. Kindl, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 629; (*b*) I. Meisel, G. Hertel and K. Weiss, *J. Mol. Catal.*, 1986, **36**, 159; (*c*) K. R. Birdwhistell, J. Lanza and J. Pasos, *J. Organomet. Chem.*, 1999, **584**, 200; (*d*) A. W. Holland and R. G. Bergman, *J. Am. Chem. Soc.*, 2002, **124**, 9010.

4 K. B. Dillon, V. C. Gibson and L. J. Sequeira, *J. Chem. Soc., Chem. Commun.*, 1995, 2429.

5 W.-D. Wang and J. H. Espenson, *Organometallics*, 1999, **18**, 5170.

6 A. A. Zhizhin, D. N. Zarubin and N. A. Ustynyuk, *Tetrahedron Lett.*, 2008, **49**, 699.

7 (*a*) K. R. Birdwhistell, T. Boucher, M. Ensminger, S. Harris, M. Johnson and S. Toporek, *Organometallics*, 1993, **12**, 1023; (*b*) R. Ghosh and A. G. Samuelson, *Chem. Commun.*, 2005, 2017.

8 Y. V. Zeifman, E. G. Ter-Gabrielyan, D. P. Del'tsova and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 396 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **28**, 366); (*b*) A. Li, S.-z. Zhu, Q.-c. Huang and J.-s. Liu, *J. Fluorine Chem.*, 1994, **68**, 145; (*c*) L. N. Markovskii, A. V. Solov'ev, N. P. Kolesnik and Yu. G. Shermolovich, *Zh. Org. Khim.*, 1995, **31**, 656 (*Russ. J. Org. Chem.*, 1995, **31**, 605); (*d*) S. V. Moiseev, V. M. Goncharov, G. V. Zatonsky, V. F. Cherstkov and N. V. Vasil'ev, *Mendeleev Commun.*, 2006, 184.

9 (*a*) G. La Monica and S. Cenini, *Inorg. Chim. Acta*, 1978, **29**, 183; (*b*) S. Cenini and M. Pizzotti, *Inorg. Chim. Acta*, 1980, **42**, 6568; (*c*) K. A. Rufanov, D. N. Zarubin, N. A. Ustynyuk, D. N. Gourevitch, J. Sundermeyer, A. V. Churakov and J. A. K. Howard, *Polyhedron*, 2001, **20**, 379; (*d*) D. N. Zaroubine, D. S. Holovko and N. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 987 (*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1075).

10 K.-M. Chang and C. O. Knowles, *J. Agric. Food Chem.*, 1977, **25**, 493.

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[§] *Condensation of* N-*sulfinylamines: general procedure*. A 100 ml Schlenk flask was charged with *N*-sulfinylamine (3 mmol), $(MesN)_2Mo(CH_2CMe_2Ph)_2$ (0.06 g, 0.09 mmol, 3 mol%) as a catalyst and heptane (25–30 ml). The reaction mixture was stirred under reflux for 5 h for **3a** and 7 h for **3b**–**d**. The reaction mixture was filtered through a Celite® pad, the solvent was removed under a reduced pressure, and the residue was recrystallised from diethyl ether (compounds **3a**,**d**) or fractionated in a vacuum (compound **3b**).

Di(2,4,6-trichlorophenyl)sulfodiimine **3a**: orange crystals, yield 0.39 g (62%); mp 101–102 °C. ^1H NMR, δ: 7.12 (s, H_{Ar}). MS, *m/z* (%): 420 $[M]^+$ (8), 385 (100), 350 (5), 313 (5), 227 (16), 190 (27), 158 (10), 109 (6). Found (%): C, 34.19; H, 0.89; N, 6.59. Calc. for $C_{12}H_4Cl_6N_2S$ (%): C, 34.24; H, 0.96; N, 6.65.

The spectral data of sulfurdiimines **3b**–**d** are given in the Online Supplementary Materials.

[¶] The reaction mechanism will be published elsewhere.

[††] Identified by comparison of spectral data with those of authentic compound. ^1H NMR, δ: 6.91 (s, 2H, H_{Ar}), 2.27 (s, 3H, *p*-Me), 2.23 (s, 3H, *o*-Me).