$MoO_2Cl_2(dmf)_2$-Catalyzed Domino Reactions of ω-Nitro Alkenes to 3,4-Dihydro-2*H*-1,4-benzothiazines and Other Heterocycles

Chandi C. Malakar, Elena Merisor, Jürgen Conrad, Uwe Beifuss*

Bioorganische Chemie, Institut für Chemie, Universität Hohenheim, Garbenstr. 30, 70599 Stuttgart, Germany
Fax +49(711)45922951; E-mail: ubeifuss@uni-hohenheim.de

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Abstract: Using the transformation of allyl 2-nitrophenyl thioethers to 3,4-dihydro-2*H*-1,4-benzothiazines as an example the reductive cyclization of ω-nitroalkenes to saturated N-heterocycles can be performed highly selective and with high yields if a combination of $MoO_2Cl_2(dmf)_2$ as a catalyst and Ph_3P as reducing agent are employed.

Key words: catalysis, domino reaction, heterocycles, nitroso ene reaction, reductive cyclization

Recently we have reported on a new reductive cyclization of ω-nitroalkenes for the efficient synthesis of saturated N-heterocycles using $(EtO)_3P$ as a reagent.[1] By employing the new domino transformation we were able to convert 2-nitrophenyl ethers **1** into 3,4-dihydro-2*H*-1,4-benzoxazines **2**, *N*-allyl 2-nitroanilines **3** into 1,2,3,4-tetrahydroquinoxalines **4**, and 1-(4-methylpent-3-enyl)-2-nitrobenzene **5** into 1,2,3,4-tetrahydroquinoline **6** (Figure 1). We assume that the domino process starts with the $(EtO)_3P$-mediated reduction of the nitro group to yield the nitroso group which then reacts as the enophile in an intramolecular ene reaction with the alkene moiety as the ene to afford a cyclic hydroxyl amine. The final step of the process is the $(EtO)_3P$-mediated reduction of the NOH group giving the corresponding saturated cyclic amine. Given our present state of knowledge we cannot exclude that the reaction involves a nitrene as an intermediate.

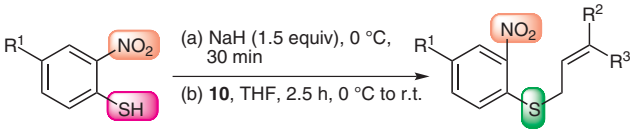
1 X = O
3 X = NR^4
5 X = CH_2
7 X = S

2 X = O
4 X = NR^4
6 X = CH_2
8 X = S

Figure 1

In order to obtain the products of the reductive cyclization with the highest possible yields it was necessary to employ a six fold excess of $(EtO)_3P$. Another problem linked to the use of $(EtO)_3P$ is the formation of N-ethylated side products originating from N-ethylation of the actual cyclization product by $(EtO)_3PO$ formed through oxidation of $(EtO)_3P$ during the course of the reaction. In many cases, however, we were able to control the formation of these side products by running the reductive cyclizations in toluene as solvent. Nevertheless we searched for alternative reagents and reaction conditions in order to decrease the excess of the reagent, to increase yields and to exclude the risk of side product formation.[2]

Herein, we report on the development of a new catalytic system based on Ph_3P as a reductant and a molybdenum complex as the catalyst. It allows for the reductive cyclization of ω-nitroalkenes to saturated N-heterocycles in high yields without interfering formation of side products. The so far unknown transformation of allyl 2-nitrophenyl thioethers **7** to 3-isopropenyl-3,4-dihydro-2*H*-1,4-benzothiazines **8** (Figure 1) was taken as an example since many heterocycles containing a 3,4-dihydro-2*H*-1,4-benzothiazine moiety are well known for their pronounced biological activity.[3]



9

88% **7a** R^1 = H, R^2 = R^3 = Me
85% **7b** R^1 = H, R^2 = Me, R^3 = H
89% **7c** R^1 = H, R^2 = R^3 = H
89% **7d** R^1 = R^2 = R^3 = Me

Scheme 1

The preparation of the allyl-2-nitrophenyl thioethers **7a–d** can be achieved easily by reacting the aromatic thiols **9**[4] with the allylic bromides **10a–c** under basic conditions in yields ranging from 85–89% (Scheme 1).[5]

To start with, the allyl-2-nitrophenyl thioether **7a** was reacted with 6 equivalents $(EtO)_3P$ under varying reaction conditions (Table 1). It was no big surprise that in most cases mixtures of **8a**, and the N-ethylated product **11a** was obtained regardless of whether the reaction was performed under reflux, in a sealed tube or under microwave conditions (Table 1, entries 1–4). Complete suppression of **11a** was possible only when the transformation was run in toluene as a solvent under microwave conditions (Table 1, entry 5).

Further experiments revealed that $(EtO)_3P$ can be replaced by Ph_3P (Table 2). Of course, the advantage of Ph_3P is that

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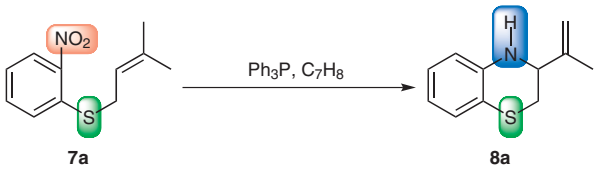
Table 1 Cyclization of **7a** with $(EtO)_3P$ under Different Reaction Conditions

7a **8a** R = H, **11a** R = Et

Entry	$(EtO)_3P$ (equiv)	Solvent	Conditions[11]	Yield of **8a** (%)[a]	Yield of **11a** (%)[a]
1	6.0	–	reflux, 157 °C, 5 h	68	5
2	6.0	–	sealed tube, 185 °C, 12 h	35	40
3	6.0	–	MW,[b] 200 °C, 0.5 h	65	8
4	6.0	C_7H_8	sealed tube, 185 °C, 12 h	64	12
5	6.0	C_7H_8	MW,[b] 200 °C, 0.5 h	74	–

[a] Isolated yield.
[b] Irradiations with microwaves were performed at 300 W and 20 bar using a Discover™ by CEM.

Table 2 Cyclization of **7a** with Ph_3P under Different Conditions



7a **8a**

Entry	Ph_3P (equiv)	Conditions	Yield of **8a** (%)[a]
1	6.0	sealed tube, 185 °C, 15 h	55
2	6.0	MW,[b] 200 °C, 0.75 h	54
3	2.4	sealed tube, 185 °C, 15 h	55
4	2.4	MW,[b] 200 °C, 1.25 h	47

[a] Isolated yield.
[b] Irradiations with microwaves were performed at 300 W and 20 bar using a Discover™ by CEM.

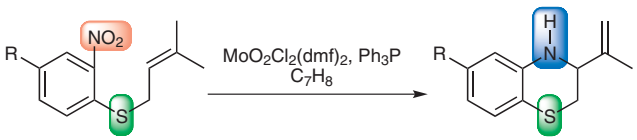
the N-ethylated product **11a** cannot occur. Another advantage is that the amount of Ph_3P can be reduced from 6.0 equivalents to 2.4 equivalents, corresponding to an excess of the reagent of only 20% (Table 2, entries 3 and 4). The problem of the formation of N-ethylated products could be solved by using Ph_3P as a reagent, but the yields of **8a** remained unsatisfactory (47–55%). Thus, further options were tested to run the reaction more efficiently. Recently, it has been reported that $MoO_2Cl_2(dmf)_2$ can be used to catalyze the Cadogan cyclization of 2-nitrobiphenyl to carbazoles with Ph_3P,[6] the deoxygenation of sulfoxides to sulfides with phosphites[7] and the reduction of *N*-oxides with Ph_3P.[8] Against this background we studied the reductive cyclization of allyl-2-nitrophenyl thioethers **7** with several P(III) reagents in the presence of catalytic amounts of $MoO_2Cl_2(dmf)_2$.[7,9]

First, the molybdenum-catalyzed reductive cyclization of **7a** with Ph_3P was studied (Table 3). When **7a** was reacted with 2.4 equivalents Ph_3P in the presence of 2 mol% $MoO_2Cl_2(dmf)_2$ as a catalyst in toluene in a sealed tube for 15 hours at 185 °C, the cyclization product **8a** was isolated in 63% (Table 3, entry 1). This result differs only slightly from that of the uncatalyzed reaction. It could be demonstrated, however, that increasing the amount of $MoO_2Cl_2(dmf)_2$ resulted in markedly improved yields. With 5 mol% $MoO_2Cl_2(dmf)_2$ the yield of **8a** amounts to 80% (Table 3, entry 2); it increases to 83% with 6 mol% $MoO_2Cl_2(dmf)_2$ (Table 3, entry 3) and can be as high as 89% when 10 mol% of the catalyst are employed (Table 3, entry 4). Then we focused on optimizing the amount of Ph_3P. It was found that reducing Ph_3P from 2.4 equivalents to 1.0 equivalent significantly decreased the yield of **8a** from 89–55% (Table 3, entries 4 and 5). When the reaction was run with 10 mol% or 250 mol% $MoO_2Cl_2(dmf)_2$ in the absence of any Ph_3P the yield of **8a** dropped dramatically to 15% and 17%, respectively (Table 3, entries 6 and 7). Due to this finding all further experiments were performed with 2.4 equivalents of Ph_3P. The reactions of **7a**,**d** with 2.4 equivalents of Ph_3P in the presence of catalytic amounts of $MoO_2Cl_2(dmf)_2$ can also be conducted under microwave conditions (Table 3, entries 8–12). Compared to the reactions performed in sealed vials under thermal conditions the reaction times were reduced markedly by employing microwave radiation. Under thermal conditions the transformation of **7a** with 10 mol% $MoO_2Cl_2(dmf)_2$ and 2.4 equivalents Ph_3P, for example, took 15 hours to run to completion; under microwave conditions, however, only 30 minutes were needed. The yields of **8a** were nearly identical under both conditions (Table 3, entries 4 and 11).

In addition to the reactions with Ph_3P a number of other P(III) compounds were tested as reducing agents. It was found that the transformations with polymer-bound Ph_3P as well as $(n\text{-}Bu)_3P$ also resulted in the selective formation of **8a**. Further experiments revealed that the $MoO_2Cl_2(dmf)_2$-catalyzed reaction of **7a** with Ph_3P cannot only be run in toluene but in other solvents as well. In addition to several aromatic solvents (benzene, mesitylene, cumene, diisopropyl benzene, and chlorobenzene) these also include some ethers (THF and 1,4-dioxane) and dipolar aprotic solvents (MeCN and DMF). It is noteworthy that the reaction does not work in polar protic solvents. As the best yields of **8a**[14] were achieved in toluene it remained the solvent of choice.

As a result, two standard procedures were developed to be applied in most of the transformations described. Accordingly, the substrate of choice was reacted with 10 mol% $MoO_2Cl_2(dmf)_2$ and 2.4 equivalents Ph_3P in toluene at 185 °C in a sealed tube or under MW conditions at 200 °C. Under these conditions the allyl thioethers **7b** and **7c** with differently substituted allyl groups were reacted (Table 4). No problems were encountered in the reductive cyclization of the (*E*)-2-butenyl thioether **7b** which afforded the corresponding vinyl derivate **8b** with yields of

Table 3 The $MoO_2Cl_2(dmf)_2$/Ph_3P-Catalyzed Cyclization of **7a**,**d**[10,12,13,14]



7a,**d** **8a**,**d**

Entry	7	$MoO_2Cl_2(dmf)_2$ (mol%)	Ph_3P (equiv)	Conditions	Yield of **8** (%)[a]
1	**7a**	2	2.4	sealed tube, 185 °C, 12 h	63
2	**7a**	5	2.4	sealed tube, 185 °C, 15 h	80
3	**7a**	6	2.4	sealed tube, 184 °C, 10 h	83
4	**7a**	10	2.4	sealed tube, 185 °C, 15 h	89
5	**7a**	10	1.0	sealed tube, 185 °C, 15 h	55
6	**7a**	10	–	sealed tube, 185 °C, 15 h	15
7	**7a**	250	–	sealed tube, 184 °C, 3 h	17
8	**7a**	6	2.4	MW,[b] 200 °C, 4 h	77
9	**7a**	6	2.4	MW,[b] 200 °C, 2 h	76
10	**7a**	6	2.4	MW,[b] 200 °C, 0.5 h	73
11	**7a**	10	2.4	MW,[b] 200 °C 0.5 h	88
12	**7d**	10	2.4	MW,[b] 200 °C, 0.5 h	76

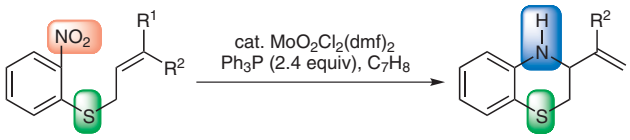
[a] Isolated yield.
[b] Irradiations with microwaves were performed at 300 W and 20 bar using a Discover™ by CEM.

69% and 68%, respectively (Table 4, entries 1 and 2). In contrast, the allyl thioether **7c** did not react at all (Table 4, entries 3 and 4).

These results indicate that the reductive cyclizations presented here follow an Alder–ene reaction mechanism since the alkene moiety of **7c** cannot act as an ene in an Alder–ene reaction.

And finally it could be demonstrated that apart from 3,4-dihydro-2*H*-1,4-benzothiazines other heterocycles can be made accessible by the catalytic system presented here (Table 5). For example, the reaction of the 2-nitrophenyl ally ether **1a** afforded the 3,4-dihydro-2*H*-1,4-benzoxazine **2a**. The cyclization can be managed in a sealed vial under both thermal and microwave conditions; **2a** was isolated with yields of 84% and 86%, respectively (Table 5, entries 1 and 2). Analogous reactions of **1b** de-

Table 4 The $MoO_2Cl_2(dmf)_2$-Catalyzed Reductive Cyclization of **7b**,**c**[10,12]



7b R^1 = Me, R^2 = H
7c R^1 = R^2 = H

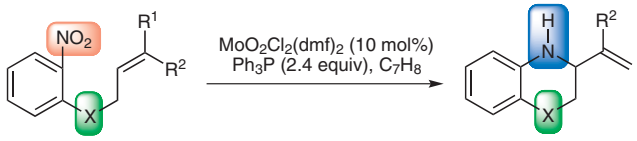
8b R^2 = H

Entry	7	$MoO_2Cl_2(dmf)_2$ (mol%)	Conditions	Product	Yield (%)[a]
1	**7b**	10	sealed tube, 185 °C, 15 h	**8b**	68
2	**7b**	10	MW,[b] 200 °C, 0.5 h	**8b**	69
3	**7c**	6	sealed tube, 185 °C, 10 h	–	–
4	**7c**	6	MW,[b] 200 °C, 0.5 h	–	–

[a] Isolated yield.
[b] Irradiations with microwaves were performed at 300 W and 20 bar using a Discover™ by CEM.

livered the 3,4-dihydro-2*H*-1,4-benzoxazine **2b** in 63% and 65% yield, respectively (Table 5, entries 3 and 4). Also, 1,2,3,4-tetrahydroquinolines **6** can be produced by reacting **5**, as could be demonstrated using the cyclizations of **5a** to **6a** as an example (Table 5, entries 5 and 6).

Table 5 The $MoO_2Cl_2(dmf)_2$-Catalyzed Reductive Cyclization of **1a**,**b** and **5a**



1a R^1 = Me, R^2 = Me, X = O
1b R^1 = Me, R^2 = H, X = O
5a R^1 = Me, R^2 = Me, X = CH_2

2a R^2 = Me
2b R^2 = H
6a R^2 = Me

Entry	Substrate	Conditions	Product	Yield (%)[a]
1	**1a**	sealed tube, 185 °C, 15 h	**2a**	84
2	**1a**	MW,[b] 200 °C, 0.5 h	**2a**	86
3	**1b**	sealed tube, 185 °C, 15 h	**2b**	63
4	**1b**	MW,[b] 200 °C, 0.5 h	**2b**	65
5	**5a**	sealed tube, 185 °C, 15 h	**6a**	64
6	**5a**	MW,[b] 200 °C, 0.5 h	**6a**	63

[a] Isolated yield.
[b] Irradiations with microwaves were performed at 300 W and 20 bar using a Discover™ by CEM.

To summarize, the efficient synthesis of 3,4-dihydro-2*H*-1,4-benzothiazines **8**, 4-dihydro-2*H*-1,4-benzoxazines **2**, and 1,2,3,4-tetrahydroquinolines **6** by reductive cyclization of the corresponding ω-nitroalkenes **7**, **1**, and **3** can be achieved by employing a catalytic system based on Ph_3P as a reductant and $MoO_2Cl_2(dmf)_2$ as a catalyst. The molybdenum-catalyzed transformations with Ph_3P are characterized by being superior to the uncatalyzed transformations with $(EtO)_3P$ in both selectivity and yields.

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References and Notes

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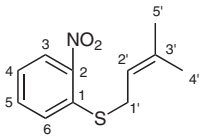
(10) **General Procedure for the Synthesis of Thioethers 7a–d**
In an oven dried 250 mL three-necked round-bottom flask 2-nitro thiophenol **9** (16.11 mmol) was dissolved in freshly distilled dry THF (50 mL) under Ar. Sodium hydride (80%) (24.16 mmol) was added in several portions at 0 °C during 10 min, and after complete addition the reaction mixture was stirred for 30 min at 0 °C. Freshly distilled allyl bromide (64.44 mmol) was added dropwise at 0 °C; after complete addition the reaction mixture was allowed to stir at r.t. for 12.5 h. Then the reaction mixture was poured into sat. NH_4Cl (100 mL) and extracted with TBME (3 × 100 mL). The combined organic phases were washed with brine (100 mL) and dried over anhyd $MgSO_4$. The solvents were removed under reduced pressure, and the crude product was purified by Kugelrohr distillation or by flash column chromatography on silica gel (cyclohexane–EtOAc, 20:1).
(11) **General Procedure for the $(EtO)_3P$-Mediated Domino Reaction under Microwave Conditions**
A 10 mL process vial was charged with a mixture of **7** (1 mmol), $(EtO)_3P$ (1.07 mL, 6 mmol) and toluene (3 mL). The vial was sealed, placed into the cavity of the microwave reactor, and irradiated with microwaves at 200 °C for 30–35 min, after removing $(EtO)_3P$ and $(EtO)_3PO$ by Kugelrohr distillation under reduced pressure, the remaining residue was diluted with hot EtOAc (50 mL). The organic phase was washed with brine (3 × 20 mL) and dried over $MgSO_4$. Solvent was removed under reduced pressure, and the remaining residue was purified by flash chromatography on silica gel (cyclohexane–EtOAc, 20:1).
(12) **General Procedure for the Mo(VI)-Catalyzed Domino Reaction under Microwave Conditions with Ph_3P as a Reagent**
A 10 mL process vial was charged with a mixture of **7** (1 mmol), Ph_3P, $MoO_2Cl_2(dmf)_2$, and toluene (3 mL). The vial was sealed, placed into the cavity of the microwave reactor, and irradiated with microwaves at 200 °C for 30–240 min, after filtration and removal of the solvent the reaction mixture was poured into H_2O (100 mL) and extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with brine (3 × 20 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. The remaining residue was purified by flash chromatography on silica gel (cyclohexane–EtOAc, 20:1). Alternatively, the reaction mixture can also be purified by flash column chromatography without any workup procedure.
(13) **Selected Data for 1-(3-Methylbut-2-enylsulfanyl)-2-nitrobenzene (7a, Figure 2)**
R_f = 0.52 (cyclohexane–EtOAc, 20:1). UV/vis (MeCN): λ_{max} (log ε) = 245 (4.20), 380 (3.43) nm. IR (ATR): 2914, 1593, 1565, 1508, 1452, 1376, 1333, 1303, 1252, 1170, 1103, 1061, 1044, 981, 852, 780, 730 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.74 (br s, 3 H, 4′-H), 1.76 (br s, 3 H, 5′-H), 3.60 (d, ^3J = 7.8 Hz, 2 H, 1′-H), 5.31 (sept, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1 H, 2′-H), 7.24 (ddd, ^3J = 7.2 Hz, ^3J = 8.2 Hz,

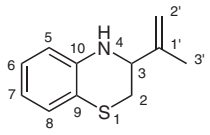
^4J = 1.4 Hz, 1 H, 4-H), 7.41 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1 H, 6-H), 7.54 (ddd, ^3J = 7.2 Hz, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1 H, 5-H), 8.19 (dd, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1 H, 3-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 18.25 (C-5′), 26.00 (C-4′), 31.27 (C-1′), 117.18 (C-2′), 124.65 (C-4), 126.33 (C-3), 127.29 (C-6), 133.61 (C-5), 138.80 (C-1), 139.03 (C-3'), 146.25 (C-2). MS (EI, 70 eV): *m/z* (%) = 223 (20) [M$^+$], 206 (5), 155 (36), 139 (100), 138 (23), 125 (8), 117 (3), 69 (1). HRMS (EI): *m/z* [M$^+$] calcd for $C_{11}H_{13}NO_2S$: 223.0667; found: 223.0664. Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; N, 6.27. Found: C, 59.18; H, 5.92; N, 6.62.



7a

Figure 2

(14) **Selected Data for 3-Isopropenyl-3,4-dihydro-2*H*-benzo[1,4]thiazine (8a, Figure 3)**
R_f = 0. 54 (cyclohexane–EtOAc, 20:1). UV/vis (C_2H_5OH): λ_{max} (log ε) = 230 (4.36), 313 (3.67) nm. IR (ATR): 3397, 2927, 1647, 1589, 1477, 1417, 1306, 1263, 1237, 1156, 1107, 1075, 1033, 957, 899, 838, 738 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83 (s, 3 H, 3′-H), 2.98 (overlapped, 1 H, 3-H), 2.98 (dd, ^3J = 3.9 Hz, ^2J = 12.5 Hz, 1 H, 2b-H), 3.04 (dd, ^3J = 7.3 Hz, ^2J = 12.5 Hz, 1 H, 2a-H), 4.08 (br dd, ^3J = 3.9 Hz, ^3J = 7.2 Hz, 1 H, 3-H), 5.03 (br s, 1 H, 2′-H), 5.11 (br s, 1 H, 2′-H), 6.54 (dd, ^3J = 8.0 Hz, ^2J = 1.3 Hz, 1 H, 5-H), 6.64 (ddd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, ^2J = 1.3 Hz, 1 H, 7-H), 6.93 (ddt, ^3J = 7.3 Hz, ^3J = 8.0 Hz, ^2J = 1.6 Hz, 1 H, 6-H), 7.02 (dd, ^3J = 7.8 Hz, ^2J = 1.5 Hz, 1 H, 8-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.22 (C-3′), 30.19 (C-2), 57.16 (C-3), 112.95 (C-2′), 115.66 (C-5), 115.88 (C-9), 118.5 (C-7), 125.93 (C-6), 127.74 (C-8), 142.01 (C-10), 145.81 (C-1′). MS (EI, 70 eV): *m/z* (%) = 191 (100) [M$^+$], 163 (18), 150 (46), 117 (21), 109 (11), 65 (5). HRMS (EI): *m/z* [M$^+$] calcd for $C_{11}H_{13}NS$: 191.0769; found: 191.0783. Anal. Calcd for $C_{11}H_{13}NS$: C, 69.07; H, 6.85; N, 7.32. Found: C, 69.15; H, 6.90; N, 7.27.



8a

Figure 3