SmI_2-mediated facile syntheses of *N*-(2,2-dichlorovinyl)amides from acetates of chloralamide

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Samarium diiodide-mediated elimination reaction provides a simple and general method to synthesise *N*-(2, 2-dichlorovinyl)amides **4** from acetates of chloralamides **3** in excellent yields. This novel reaction proceeds readily within a few minutes at room temperature.

Keywords: samarium diiodide, N-(2,2-dichlorovinyl)amides, chloralamide, reduction

As a special sort of nucleophilic reagent,[1-2] *N*-(2, 2-dichlorovinyl)amides **4** have been synthesised by several methods. Morever, using *N*-(2,2-dichlorovinyl)amides **4** as precursors for the synthesis of otherwise unattainable heterocyclic compounds has also attracted some attention.[3-4] For the synthesis of *N*-(2,2-dichlorovinyl)amides **4**, chloralamides and their derivatives have been used as common starting materials. On the other hand, we have also noted that in all these reactions electrochemical methods have been investigated in preference to pure chemical approaches and that no synthetic methods are practically satisfactory.[5-6] Previously, zinc metal was used to promote the reductive elimination reaction from chloralamides under thermal condions.[7] In this case, however, excessive zinc metal was used and there were low yields. More recently, a novel electrochemical method was also investigated for the preparation of *N*-(2, 2-dichlorovinyl)amides **4** and some progress was achieved.[8] For example, the mildness of the reaction conditions as well as its efficiency are noteworthy features of this approach. In this reaction, however, the chlorination of chloralamide **1** needs harsh reaction conditions, which lowers the reaction's attractiveness. In view of this, the development of an efficient and alternative method for the synthesis of these compounds is still desirable.

As a powerful, versatile, and ether-soluble one-electron transfer reducing agent, SmI_2 has played an ever-increasing role in organic synthesis.[9] Among many other methods, SmI_2-mediated reductive elimination is a powerful method for the synthesis of alkenes and has been extensively developed.[10] To the best of our knowledge, an SmI_2-mediated procedure for the preparation of *N*-(2,2-dichlorovinyl)amides **4** has not yet been reported. Herein, we wish to report a facile synthesis of *N*-(2,2-dichlorovinyl)amides **4** from acetates of chloralamides **3** promoted by SmI_2 in THF at room temperature.

During a previous study, we found that samarium diiodide can efficiently promote the reductive elimination of trichloromethyl carbinols to form vinyl chlorides.[11] Thus, as analogous species, chloralamide may be expected to undergo the same process in the presence of SmI_2. Firstly, chloralamide **1a** (from benzamide) was reacted with a solution of SmI_2 in THF (Scheme 1). Unfortunately, only the dehalogenation product **2a** was afforded as the major product in about 70% yield and hardly any desired product **4a** was produced.

This fact indicated that the direct elimination of the hydroxy group was not occuring and that a better leaving group was needed. Thus, we turned to another synthetic route and tried using the acetates of chloralamide **3** as the substrate under the same reaction condition.

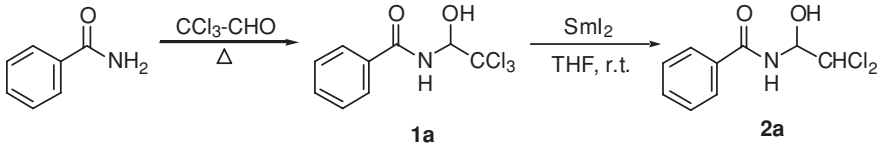
To our delight, acetates of chloralamide **3** underwent the elimination process easily to produce the *N*-(2,2-dichlorovinyl) amides **4** (Scheme 2). To investigate the scope and generality of the reaction, a number of aromatic and aliphatic (entry 8) substrates were used in this reaction, and the results were summarised in Table 1. As shown in Table 1, *N*-(2, 2-dichlorovinyl)amides **4** were produced in nearly quantitative yields from the acetates **3**. It should be noted that the reaction proceed smoothly at room temperature and finished within five minutes.

As for the reaction mechanism, the reaction could be explained as proceeding by a six-membered ring transition state. According to the literature,[10] chelation of Sm(III) with the carbonyl oxygen of the acetoxy group produces a six-membered ring (Scheme 3). Elimination from intermediate **I** would afford vinyl dichlorides, *N*-(2,2-dichlorovinyl)amides.

Table 1 SmI_2-mediated synthesis of *N*-(2,2-dichlorovinyl)amides **4** from the acetates of chloralamides **3**[a]

Entry	R	Product[b]	M. p. /°C (lit m. p. /°C	Time min	Yield %[c]
1	C_6H_5	**4a**	62–63 (64 [8])	5	97
2	*p*-$CH_3C_6H_4$	**4b**	100-102 (103 [8])	5	99
3	*o*-$CH_3C_6H_4$	**4c**	57–58 (57–59 [8])	5	95
4	*p*-ClC_6H_4	**4d**	96–98 (96–97 [8])	5	94
5	*o*-ClC_6H_4	**4e**	48–50 (49–51 [8])	5	91
6	*p*-$CH_3OC_6H_4$	**4f**	103 (102–104[8])	5	98
7	*p*-FC_6H_4	**4g**	69–70	5	99
8	CH_3CH_2	**4h**	59–60 (59[8])	15	90

[a]All reactions were carried out with 2.2 equiv. SmI_2 in a solution of THF.
[b]All products were characterised by ^1H NMR, IR and MS.
[c]Isolated yields based on acetates of chloralamides **3**.



1a **2a**

Scheme 1

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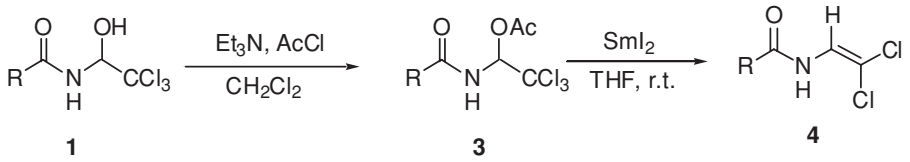
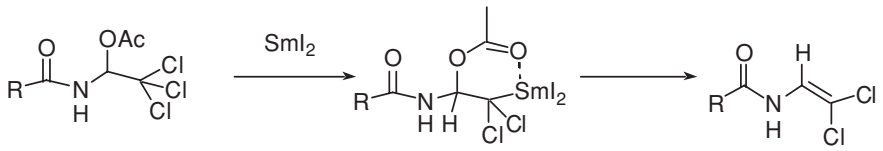


1 **3** **4**

Scheme 2



I

Scheme 3

In conclusion, we have provided a new synthesis of *N*-(2, 2-dichlorovinyl)amides **4** from the acetates of chloralamide **3**. As a novel synthetic method, the present route has a unique superiority. In view of its efficiency, experimental simplicity, excellent yields and mild reaction conditions as well as short reaction times, the present method can be a good alternative to the traditional methods and has high potential for practical applications.

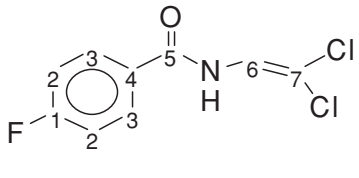
Experimental

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. ^{1}H NMR spectra were recorded on a Bruker AC-400 instrument in $CDCl_3$ solutions using TMS as an internal standard. Chemical shifts (δ) were reported in ppm and coupling constants *J* are given in Hz. IR spectra were taken as thin films with a Bruker Vector-22 infrared spectrometer. Mass spectra were obtained on a HP 5989B mass spectrometer. Elemental analyses were performed on a EA-1110 instrument. Metallic samarium and all solvents were purchased from commercial sources and were used without further purification. The starting materials chloralamides **1** were prepared from chloral hydrate and amides according to the literature.[8]

General procedure for the synthesis of acetates of chloralamide (**3**): To a solution of chloralamide **3** (2 mmol) in CH_2Cl_2 (30 ml), triethylamine (3 mmol) and CH_3COCl (3 mmol) were added dropwise at 0–10 °C with stirring. Then the mixture was warmed up to room temperature and stirred at room temperature for 3 h. After the reaction was completed, H_2O (10 ml) was added and the organic layer was separated, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by recrystallisation to give white crystals.

General procedure for the synthesis of N-(2,2-dichlorovinyl)amides (**4**): A solution of an acetate of chloralamide **3** (1 mmol) in dry THF (3 ml) was added to the solution of SmI_2 (2.2 mmol) in THF (20 ml) at room temperature under a nitrogen atmosphere. After being stirred for about 5 minutes, the deep blue colour of the solution changed to yellow rapidly. The reaction mixture was then quenched with 0.1 M hydrochloric acid (5 ml) and extracted with ether (3 × 20 ml). The organic phase was successively washed with brine (15 ml) and water (20 ml) and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude products, which were purified by preparative TLC using ethyl acetate and cyclohexane (1:4) as eluent.

N-(2,2-dichlorovinyl)-4-fluorobenzamide (**4g**): White needles, m. p. 69–70 °C. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm): 7.18–7.22 (m, 2H), 7.51 (d, 1H, J = 10.8 H_Z), 7.69 (d, 1H, J = 10.8 H_Z), 7.85–7.88 (m, 2H). ^{13}C NMR (200 MHz , $CDCl_3$) δ_H (ppm):166.69 (C-1), 164.16 (C-1), 162.38 (C-5), 129.78 (C-3), 129.68 (C-3), 128.63 (C-4), 128.60 (C-4), 121.71 (C-6), 116.26 (C-2), 116.04 (C-2),



107.43 (C-7). ν_{max}/(cm^{-1}): 3347, 3084, 1645, 1603, 1514, 1479, 1257, 850, 759. *m/z* (%) 233 (M^+, 5.2), 123 (100), 95 (53). ($C_9H_6Cl_2FNO$ requires C, 46.18; H, 2.58%. Found: C, 46.26; H, 2.40%)

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