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Anchimeric Assistance in the Rearrangement of Dichloro-3-methyl-1,4-oxathianes to 2-Chloromethyl Dihydro-1,4-oxathiins

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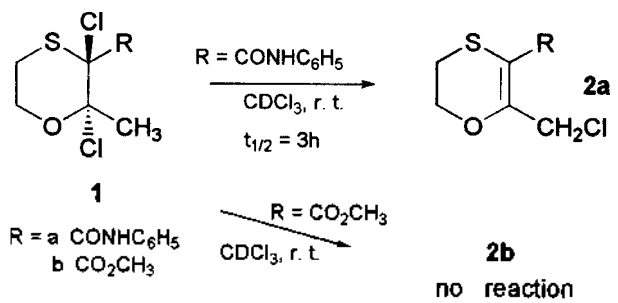
An anchimeric assistance of anilide in the rearrangement of dichloro-1,4-oxathaines **1** to 2-chloromethyl dihydro-1,4-oxathiins **2** is described. The inductive effect of the carbonyl group of anilide was negligible in the rearrangement. A rate of the rearrangement depended on the basicity of anilide nitrogen. A hydrogen bonding between the anilide hydrogen and an oxygen atom of those substituents make the nitrogen less basic, resulting in the slower rearrangement.

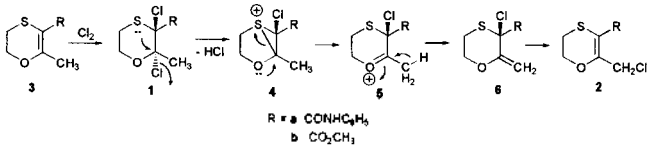
Introduction

A neighboring group participation by a heteroatom or heterosubstituent at a remote position from the reaction center is a well-known phenomenon that generally enhances the reactivity of certain classes of reactions.[1] In our previous paper,[2] we reported that dichloro-1,4-oxathiane anilide **1a** was gradually ($t_{1/2}$=3h) rearranged to chloromethyl compound **2a** at room temperature while the corresponding ester **1b** was fairly stable under the same reaction condition. As an extension of our studies on the reactivity of the dichloro-1,4-oxathianes **1** we now report an anchimeric assistance of anilide in the rearrangement.



Results and Discussion

Syntheses of starting materials, dihydro-1,4-oxathiins **3** were achieved by the previously known method.[3] Chlorination of **3** either by sulfuryl chloride or by chlorine in methylene chloride at 0 °C gave the dichloro-1,4-oxathiane **1** in quantitative yield. The ester dichloride **1b** was fairly stable at room temperature. In contrast, we were unable to isolate the probable intermediate dichloride anilide **1a** as a pure compound but immediately after work-up there were present in the ^{1}H NMR spectrum of the crude reaction mixture a methyl signal, NH, and four methylene hydrogens (ABCD spin patterns) assignable to the structure of this compound. The anilide dichloride **1a** was gradually converted to the chloromethyl compound **2a**. The plausible mechanism of the rearrangement is shown in Scheme 1.



Scheme 1

Table 1. Rearrangement of Dichloro-1,4-oxathianes **1** to Chloromethyl Compounds **2** in $CDCl_3$

entry	R	temp (°C)	time (h)	results
1	$CONHC_6H_5$	25		$t_{1/2}$=3h
2	CO_2CH_3	25	72	no reaction
3	CO_2CH_3	50		$t_{1/2}$=32h
4	$CON(CH_3)C_6H_5$	25		$t_{1/2}$=20 min
5	$CONH_2$	25		$t_{1/2}$=4h
6	H	50	68	10% conversion
7	$CONHC_6H_4(COCH_3$-o)	25	70	no reaction
8	$CONHC_6H_4(COCH_3$-o)	50		$t_{1/2}$=18h
9	$CONHC_6H_4(COCH_3$-p)	25	6	41% conversion
10	$CONHC_6H_4(OCH_3$-o)	25	2	5% conversion
11	$CONHC_6H_4(OCH_3$-p)	25	2	44% conversion
12	$CONHC_6H_4(NO_2$-o)	25	24	no reaction
13	$CONHC_6H_4(NO_2$-p)	25	2	34% conversion

The sulfur is postulated to attack the anomeric halo carbon of **1** to give thiiranium ion **4** which would be converted to exomethylene intermediate **6** *via* low energy oxonium ion **5**. Allylic rearrangement of the exomethylene **6** produced the chloromethyl compound **2**. Interestingly, the stability of the dichloride **1** was dramatically depended on the substituent R on C-3 (Table 1). The reaction progress was quantitatively monitored by ^{1}H NMR by following the appearance of the chloromethyl peak in **2** as well as disappearance of the methyl peak of the dichloride **1**. The chloromethyl compound had identical ^{1}H NMR and IR spectra with those of compound obtained either by the previously reported method[4] or by allylic chlorination with *N*-chlorosuccinimide (see the experimental section).

Inductive effect of the carbonyl group on C-3 of the **1** would lower the lone paired electron density on the sulfur atom, reducing the effect of the neighboring group participation of the sulfur on anomeric carbon. However, the dichloro-1,4-oxathaines without carboxanilide group (entry 6) were more stable than the ester (entry 2, 3) or amide (entry 1), revealed that the inductive effect of the carbonyl is negligible in the rearrangement. It was suggested that a C-3 substituent can speed up the conversion of the dichloride to chloromethyl compound. More facile rearrangement of anilide (entry 1) in comparison with the ester (entry 2) could be explained by the larger extent of anchimeric assistance of amides than that of esters.[5] N-methyl group (entry 4) made the nitrogen more basic to promote the elimination of hydrogen in methyl of oxonium ion **5**. An important feature was observed for anilide with an acetyl (entry 7, 8), a methoxy (entry 10), or nitro substituent (entry 12) in ortho position in the aromatic nucleus. The stability of the dichloride anilide with an acetyl (entry 9), a methoxy (entry 11), or a nitro substituent (entry 13) in para position in the phenyl group was similar to that of the unsubstituted anilide (entry 1), which can be accounted for in terms of a hydrogen bonding effect rather than of the steric or the resonance effect involving aromatic nucleus. The hydrogen bond between the anilide hydrogen and an oxygen atom of those substituents was proven by their ^{1}H NMR spectra. Thus, the downfield shift of their NH proton of dihydro-1,4-oxathiin

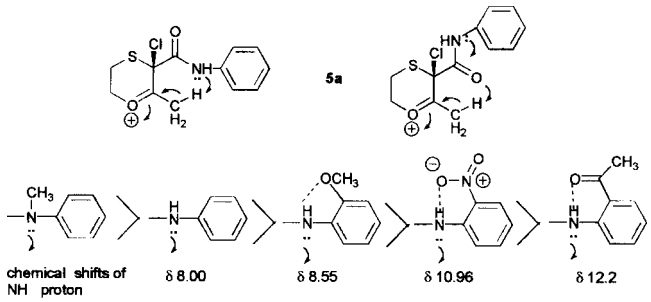
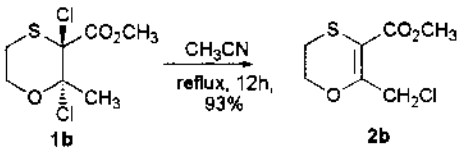


Figure 1. Relative basicity of nitrogen in the rearrangement of dichloro-1,4-oxathianes **1** to chloromethyl compound **2** through **5a**.



Scheme 2

derivatives (δ 12.2 ppm for ortho acetyl, δ 8.55 ppm for ortho methoxy, and δ 10.96 ppm for ortho nitro) in comparison with that of unsubstituted anilide (δ 8.00 ppm) suggests a strong hydrogen bonding is present in them. The unexpected stability of the ortho acetyl (entry 7), the ortho nitro dichloride (entry 12) in comparison with the ortho methoxy dichloride (entry 10) is attributable to the stronger hydrogen bond, illustrated in downfield shift of NH proton of their ^{1}H NMR as described above (Figure 1). The lone paired electron density of the nitrogen would attracted by the hydrogen bonding, resulted in lower basicity than the unsubstituted anilide, resulting in the slower rearrangement. The ideally located amide nitrogen is effecting removal of a methyl hydrogen. The alternative mechanism involving the carbonyl oxygen may be considered.

As expected, the ester dichloride **1b** was converted smoothly to the corresponding chloromethyl ester **2b** under drastic conditions, e.g. in refluxing acetonitrile (12h, 93% conversion) (Scheme 2).

Experimentals

Melting points were determined on a Thomas-Hoover capillary melting point apparatus. All ^{1}H NMR spectra were recorded either on a Varian EM360 spectrometer or Varian Gemini 300 spectrometer. Chemical shifts (δ) are in ppm and coupling constants (J) are in Hz. IR spectra were obtained on a Perkin-Elmer 16F-PC FT-IR and are reported in cm^{-1}. Elemental analyses of new compounds were performed using a Fisons EA1108 analyzer. All chromatographic isolation was accomplished on silica gel GF254 (70-230 mesh).

Synthesis of 5,6-Dihydro-2-methyl-1,4-oxathiin-3-carboxamides, 3 (General procedure)

A mixture of methyl 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylate[3] (8.7 g, 50 mmol) and potassium hydroxide (8.4 g) dissolved in water (30 mL) was refluxed for 1h. The reaction mixture cooled, washed with methylene chloride, and acidified with concentrated hydrochloric acid until the

pH reached 2-3. The precipitates was washed with cold water, and then dried to give 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylic acid as a light yellow solid (5.2 g, 65%). A suspended solution of the carboxylic acid (320 mg, 2 mmol) and thionyl chloride (160 μL, 2.2 mmol) in benzene (10 mL) was refluxed for 1h. The solvent was removed under reduced pressure to give a light yellow oily residue. This acyl chloride diluted with benzene (10 mL) was treated with either anilines or ammonia water (5 mmol) at room temperature for overnight. The precipitates were filtered off, and the filtrate was washed sequentially with diluted hydrochloric acid, 0.1 N sodium hydroxide solution, water, and then dried ($MgSO_4$). Evaporation of solvent gave the corresponding dihydro-1,4-oxathiin-3-carboxamide (78-85%).

Methyl 5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxylate. mp 58-60 °C; ^{1}H NMR 2.27 (s, CH_3), 2.88 (m, CH_2S), 3.67-3.72 (m, OCH_3), 4.27-4.32 (m, CH_2O), IR 1700 (C=C), 1580 (C=C). Anal Calcd for $C_7H_{10}O_3S$, Calcd C, 48.26, H, 5.79, S, 18.40, Found, C, 48.53, H, 6.10.

5,6-Dihydro-2-methyl-1,4-oxathiin-3-carboxylic acid. mp 180-181 °C; ^{1}H NMR 2.30 (s, CH_3), 2.83-3.03 (m, 5-CH_2), 4.30-4.47 (m, 6-CH_2), 7.23 (br s, OH). IR 1672 (C=O), 1556, 1290, 1088.

5,6-Dihydro-2-methyl-*N*-phenyl-1,4-oxathiin-3-carboxamide. mp 93-95 °C; ^{1}H NMR 2.22 (s, CH_3), 2.85-3.02 (m, 5-CH_2), 4.28-4.45 (m, 6-CH_2), 7.00-7.65 (m, ArH), 8.00 (br s, NH).

5,6-Dihydro-2,*N*-dimethyl-*N*-phenyl-1,4-oxathiin-3-carboxamide. mp 111-114 °C; ^{1}H NMR 1.71 (s, CH_3), 2.63-2.71 (m, 5-CH_2), 3.28 (s, N-CH_3), 3.96-4.12 (m, 6-CH_2), 7.18-7.30 (m, ArH).

5,6-Dihydro-2-methyl-1,4-oxathiin-3-carboxamide. mp 172-174 °C; ^{1}H NMR 2.27 (s, 2-CH_3), 2.90-3.05 (m, 5-CH_2), 4.30-4.43 (m, 6-CH_2), 5.76 (br s, NH_2).

5,6-Dihydro-2-methyl-*N*-(2-acetylphenyl)-1,4-oxathiin-3-carboxamide. mp 123-124 °C; ^{1}H NMR 2.26 (s, 2-CH_3), 2.68 (s, $COCH_3$), 3.04-3.08 (m, 5-CH_2), 4.36-4.42 (m, 6-CH_2), 7.09-8.78 (m, ArH), 12.06 (br s, NH).

5,6-Dihydro-2-methyl-*N*-(4-acetylphenyl)-1,4-oxathiin-3-carboxamide. mp 127-128 °C; ^{1}H NMR 2.17 (s, 2-CH_3), 2.57 (s, $COCH_3$), 2.98-3.01 (m, 5-CH_2), 4.41-4.44 (m, 6-CH_2), 7.63 and 7.94 (2d, *J*=8.8, ArH), 8.16 (br s, NH).

5,6-dihydro-2-methyl-*N*-(2-methoxyphenyl)-1,4-oxathiin-3-carboxamide. mp 122-125 °C; ^{1}H NMR 2.27 (s, 2-CH_3), 2.76-3.01 (m, 5-CH_2), 3.87 (s, OCH_3), 4.27-4.42 (m, 6-CH_2), 6.75-8.40 (m, ArH), 8.55 (br s, NH).

5,6-Dihydro-2-methyl-*N*-(4-methoxyphenyl)-1,4-oxathiin-3-carboxamide. mp 114-115 °C; ^{1}H NMR 2.25 (s, 2-CH_3), 2.88-3.02 (m, 5-CH_2), 3.78 (s, OCH_3), 4.30-4.45 (m, 6-CH_2), 6.82 and 7.42 (2d, *J*=9.6, ArH), 7.82 (br s, NH).

5,6-Dihydro-2-methyl-*N*-(2-nitrophenyl)-5,6-dihydro-1,4-oxathiin-3-carboxamide. mp 122-124 °C; ^{1}H NMR 2.27 (s, 2-CH_3), 2.91-3.07 (m, 5-CH_2), 4.33-4.50 (m, 6-CH_2), 6.97-8.90 (m, ArH), 10.96 (br s, NH).

5,6-Dihydro-2-methyl-*N*-(4-nitrophenyl)-1,4-oxathiin-3-carboxamide. mp 139-143 °C; ^{1}H NMR 2.27 (s, 2-CH_3), 2.90-3.05 (m, 5-CH_2), 4.33-4.50 (m, 6-CH_2), 7.70 and 8.20 (2d, *J*=9, ArH), 8.35 (br s, NH).

2,3-Dihydro-6-methyl-1,4-oxathiin. oily liquid; ^{1}H NMR 1.86 (s, CH_3), 2.86-3.06 (m, 5-CH_2), 4.30-4.47 (m, 6-CH_2), 4.87 (s, 3-CH).

Synthesis of Dichloro-1,4-oxathiane, 1 (General Procedure)

To a stirred solution of 5,6-dihydro-1,4-oxathiin (10 mmol) in methylene chloride (40 mL) cooled in an ice bath was added dropwise a solution of chlorine (11 mmol) dissolved in methylene chloride (28 mL) over 10 min, and the reaction mixture was allowed to stir at the same temperature for 10 min, and the solvent was removed under reduced pressure to obtain dichloro-1,4-oxathiane in quantitative yields.

Methyl 2,3-Dichloro-2-methyl-1,4-oxathiane-3-carboxylate. mp 57-59 °C; ^{1}H NMR 2.20 (s, 2-CH_3), 2.51 (m, *J*=2.3, *J*=2.1, *J*=14.1, 5-CH (equatorial)), 3.41 (m, *J*=12.4, *J*=3.6, 5-CH (axial)), 3.89 (s, OCH_3), 4.14 (m, *J*=12.2, 6-CH (equatorial)), 4.35 (m, 6-CH (axial)); IR (KBr) 1745 (C=O). Anal Calcd for $C_7H_{10}O_3SCl_2$; C, 34.30; H, 4.11. Found C, 34.15; H, 4.09.

2,3-Dichloro-2-methyl-*N*-phenyl-1,4-oxathiane-3-carboxamide. (obtained as a transient intermediate): ^{1}H NMR 2.15 (s, 2-CH_3), 2.62-2.67 and 3.50-3.60 (m, 5-CH_2), 4.16-4.21 and 4.44-4.53 (m, 6-CH_2), 7.16-7.56 (m, ArH), 8.14 (br s, NH).

2,3-Dichloro-5,6-dihydro-2-methyl-1,4-oxathiane-3-carboxamide. oil; ^{1}H NMR 2.13 (s, 2-CH_3), 2.38-2.49 and 3.13-3.80 (2m, 5-CH_2), 3.93-4.70 (m, 6-CH_2), 6.16 (br s, NH_2).

2,3-Dichloro-*N*-(2-acetylphenyl)-2-methyl-1,4-oxathiane-3-carboxamide. oil; ^{1}H NMR 2.18 (s, 2-CH_3), 2.67 (s, $COCH_3$), 2.61-2.69 and 3.50-3.58 (m, 5-CH_2), 4.15-4.20 and 4.43-4.50 (m, 6-CH_2), 7.18-8.74 (m, ArH), 12.77 (br s, NH).

2,3-Dichloro-*N*-(4-acetylphenyl)-2-methyl-1,4-oxathiane-3-carboxamide. mp 141-141.5 °C; ^{1}H NMR 2.15 (s, 2-CH_3), 2.59 (s, $COCH_3$), 2.65-2.70 and 3.52-3.61 (m, 5-CH_2), 4.18-4.23 and 4.49-4.54 (m, 6-CH_2), 7.64 and 7.97 (2d, *J*=8.7, ArH), 8.80 (br s, NH).

2,3-Dichloro-*N*-(2-methoxyphenyl)-2-methyl-1,4-oxathiane-3-carboxamide. mp 88 °C; ^{1}H NMR 2.17 (s, 3H, 2-CH_3), 2.40-2.87 and 3.20-3.80 (2m, 5-CH_2), 3.93 (s, OCH_3), 4.12-4.73 (m, 6-CH_2), 6.73-8.43 (m, ArH), 8.95 (br s, NH).

2,3-Dichloro-*N*-(4-methoxyphenyl)-2-methyl-1,4-oxathiane-3-carboxamide. oil; ^{1}H NMR 2.10 (s, 2-CH_3), 2.40-2.76 and 3.20-3.90 (2m, 5-CH_2), 3.92-4.04 (m, 6-CH_2), 3.75 (s, OCH_3), 6.80 and 7.38 (2d, *J*=9.0, ArH), 8.00 (br s, NH).

2,3-Dichloro-5,6-dihydro-*N*-(2-nitrophenyl)-2-methyl-1,4-oxathiane-3-carboxamide. mp 90-92 °C; ^{1}H NMR 2.17 (s, 2-CH_3), 2.66-2.70 and 3.50-3.60 (2m, 5-CH_2), 4.17-4.22 and 4.43-4.52 (2m, 6-CH_2), 7.26-8.73 (m, ArH), 11.48 (br s, NH).

2,3-Dichloro-5,6-dihydro-2-methyl-*N*-(4-nitrophenyl)-1,4-oxathiane-3-carboxamide. oil; ^{1}H NMR 2.13 (s, 2-CH_3), 2.47-2.83 and 3.27-3.82 (2m, 5-CH_2), 3.97-4.47 (m, 6-CH_2), 7.70 and 8.23 (2d, *J*=10.0, ArH), 8.47 (br s, NH).

2,3-Dichloro-2-methyl-1,4-oxathiane. ^{1}H NMR 2.00 (s, 2-CH_3), 2.34-2.39 and 3.42-3.48 (2m, 5-CH_2), 3.97-4.53 (m, 6-CH_2) 5.13 (s, 3-CH).

Rearrangement of Dichloro-3-methyl-1,4-oxathianes, 1 to 2-Chloromethyl Dihydro-1,4-oxathiins, 2 in $CDCl_3$ (General Procedure)

To a stirred solution of 5,6-dihydro-1,4-oxathiin **3** (10 mmol) in methylene chloride (40 mL) cooled in an ice bath was added dropwise a solution of chlorine (11 mmol) dissolved in methylene chloride (28 mL) over 10 min, and the reaction mixture allowed to stir at the same temperature for 10 min, the solvent was removed quickly under reduced pressure to obtain dichloro-1,4-oxathiane **1** in quantitative yields. The dichloro-1,4-oxathiane **1** (about 20 mg) dissolved in $CDCl_3$ (0.7 mL) was put in NMR tube, and then placed in oil bath either under 25 °C or under 50 °C. The reaction progress was quantitatively monitored as a function of time by means of ^1H NMR by following the appearance of the chloromethyl peak in **2** as well as disappearance of the methyl peak of the dichloride **1**.

Independent Synthesis of Chloromethyl Compound, 2 (General Procedure)

A suspended solution of dihydro-1,4-oxathiin **3** (10 g, 42.5 mmol), N-chlorosuccinimide (6.25 g) and benzoyl peroxide (400 mg) in carbon tetrachloride (100 mL) was refluxed for 10 min. After the reaction mixture was cooled under the ice bath, the precipitates were filtered off. The solvent was removed to give light yellow oily residue (8.9 g, 77.6%). Crystallization from a mixture of methylene chloride and petroleum ether afforded **2**.

Methyl 2-Chloromethyl-5,6-dihydro-1,4-oxathiin-3-carboxylate. oil; ^1H NMR 2.99-3.03 (m, 5-CH_2), 3.80 (s, 3-OCH_3), 4.40-4.43 (m, 6-CH_2), 4.64 (s, CH_2Cl).

2-Chloromethyl-5,6-dihydro-*N*-phenyl-1,4-oxathiin-3-carboxamide. mp 104-106 °C; ^1H NMR 3.04-3.07 (m, 5-CH_2), 4.43-4.47 (m, 6-CH_2), 4.53 (s, CH_2Cl), 7.10-7.57 (m, ArH), 7.93 (br s, NH).

2-Chloromethyl-5,6-dihydro-*N*-methyl-*N*-phenyl-1,4-oxathiin-3-carboxamide. mp 130-133 °C; ^1H NMR 2.69-2.80 (m, 5-CH_2), 3.36 (s, N-CH_3), 4.10-4.21 (m, 6-CH_2), 4.21 (s, CH_2Cl), 7.20-7.70 (m, ArH), Anal Calcd for $C_{13}H_{14}NSClO_2$: C, 55.02; H, 4.97, N, 4.94, S, 11.30, Cl, 12.49. Found: C, 55.07, H, 4.99; N, 4.87.

2-Chloromethy-5,6-dihydro-1,4-oxathiin-3-carboxamide. ^1H NMR 2.92-3.18 (m, 5-CH_2), 4.33-4.50 (m, 6-CH_2), 4.53 (s, CH_2Cl), 7.26 (br s, NH_2).

2-Chloromethyl-*N*-(2-acetylphenyl)-5,6-dihydro-1,4-oxathiin-3-carboxamide. mp 150-151 °C; ^1H NMR 2.67 (s, $COCH_3$), 3.09-3.12 (m, 5-CH_2), 4.44-4.57 (m, 6-CH_2), 4.53 (s, CH_2Cl), 7.14-8.76 (m, ArH), 12.20 (br s, NH).

2-Chloromethyl-*N*-(2-acetylphenyl)-5,6-dihydro-1,4-oxathiin-3-carboxamide. mp 149-149.5 °C; ^1H NMR 2.53 (s, $COCH_3$), 3.07-3.09 (m, 5-CH_2), 4.48-4.51 (m, 6-CH_2), 4.54 (s, CH_2Cl), 7.66 and 7.96 (2d, *J*=8.6, ArH), 8.12 (br s, NH).

2-Chloromethyl-*N*-(2-methoxyphenyl)-5,6-dihydro-1,4-oxathiin-3-carboxamide. ^1H NMR 2.92-3.08 (m, 5-CH_2), 3.76 (s, OCH_3), 4.31-4.48 (m, 6-CH_2), 4.45 (s, CH_2Cl), 6.80 and 7.40 (2d, *J*=9.0, ArH), 7.90 (br s, NH).

2-Chloromethyl-*N*-(4-methoxyphenyl)-5,6-dihydro-1,4-oxathiin-3-carboxamide. mp 131-134 °C; ^1H NMR 2.93-3.10 (m, 5-CH_2), 3.77 (s, OCH_3), 4.33-4.47 (m, 6-CH_2), 4.50 (s, CH_2Cl), 6.83 and 7.43 (2d, ArH), 7.87 (br s, NH).

2-Chloromethyl-*N*-(4-nitrophenyl)-5,6-dihydro-1,4-oxathiin-3-carboxamide. mp 161-167 °C; ^1H NMR 3.03-3.20 (m, 5-CH_2), 4.47-4.60 (m, 6-CH_2), 4.55 (s, 2-CH_2Cl), 7.75 and 8.27 (2d, ArH), 8.30 (br s, NH).

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