REACTIONS OF AZEPINE AND DIAZEPINE DERIVATIVES WITH CHLOROSILANES IN THE PRESENCE OF MAGNESIUM: 4,5-DOUBLE ADDITION REACTIONS TO AZEPINE DERIVATIVES

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Abstract — The reactions of 1-ethoxycarbonyl-1H-azepine (1) and chlorosilanes (Xa-c) in HMPA in the presence of magnesium afforded 1:2 adducts, trans-4,5-disubstituted-4,5-dihydroazepines (2a-c), which upon heating gave siloxane derivatives (3a-b) almost quantitatively. In the same reactions with 1-ethoxycarbonyl-1H-1,2-diazepine (8), a nitryl compound (9) was obtained. The dihydroazepines and the nitryl compound are considered to be formed via radical anions 5 and 10, respectively.

Addition reactions of chlorosilanes with olefins in the presence of magnesium in hexamethylphosphoramide (HMPA) have been attracting much attention because of synthetic utility for providing variable organosilanes.[2] 1,4-Double additions take place in the reactions of chlorosilanes with 1,3-dienes, and an interesting bicyclic product is obtained in the reaction with cyclooctatetraene.[3] However, no such reactions with azepine or diazepine derivatives have been reported.

We investigated the reactions of 1-ethoxycarbonyl-1H-azepine (1) and 1-ethoxycarbonyl-1H-1,2-diazepine (8) with chlorosilanes (Xa-c), in which 1:2 adducts (trans-4,5-disubstituted-4,5-dihydroazepines, 2a-c) and a nitryl compound (9) were obtained, respectively. We wish here to report the outline of these reactions.

When 1-ethoxycarbonyl-1H-azepine (1) and 2.5 mol equiv. of dimethyldichlorosilane (Xa) were reacted in the presence of 1.5 mol equiv. of magnesium in HMPA at r. t. for 16 hr, a 1:2 adduct (2a, mp 100°C) was obtained in 35 % yield. Under the same conditions as above, 1 reacted with diphenyldichlorosilane (Xb) and trimethylchlorosilane (Xc) to give the same type of adducts (2b, oil and 2c, oil) in 54 and 40 % yields, respectively. Upon heating, the adducts 2a and 2b gave the siloxane derivatives 3a (oil) and 3b (mp 175°C) in almost quantitative yields, respectively. The NMR spectral data of these products are summarized in the Table, and the other spectral data are shown below.[4]

Table. NMR Spectral Data of 2 and 3

	Chemical Shifts (δ ppm)								Coupling Constants (Hz)	
	Ester		SiMe	OH	SiPh	H_a	H_b	H_c	J_{ab}	J_{bc}
	CH_3	CH_2		(2H)	(20H)	(2H)	(2H)	(2H)		
2a 1)	1.4	4.3	0.1 (s, 6H) 0.2 (s, 6H)	3.4		2.2 (d)	5.2 (t)	6.7 (d)	10	10
2b 2)	1.1	4.0		3.4	7.1-7.8	2.7 (d)	4.9 (t)	6.4 (d)	9	11
2c 2)	1.3	4.1	0.1 (s, 12H)			1.8 (d)	4.9 (t)	6.6 (d)	10	12
3a 2)	1.4	4.3	0.2 (s, 6H) 0.3 (s, 6H)			2.1 (ms)	5.1 (md)	6.7 (md)	ca. 2	10
3b 1)	1.2	4.1			7.1-7.8	2.8 (ms)	5.2 (md)	6.6 (md)	ca. 2	10

1) measured in $CDCl_3$. 2) measured in CCl_4.

s: singlet. d: doublet. t: triplet. ms: multiple singlet.

md: multiple doublet.

2a; UV (EtOH): 240 nm (log ε, 4.1); IR (KBr): 3400, 1730 cm^{-1}.

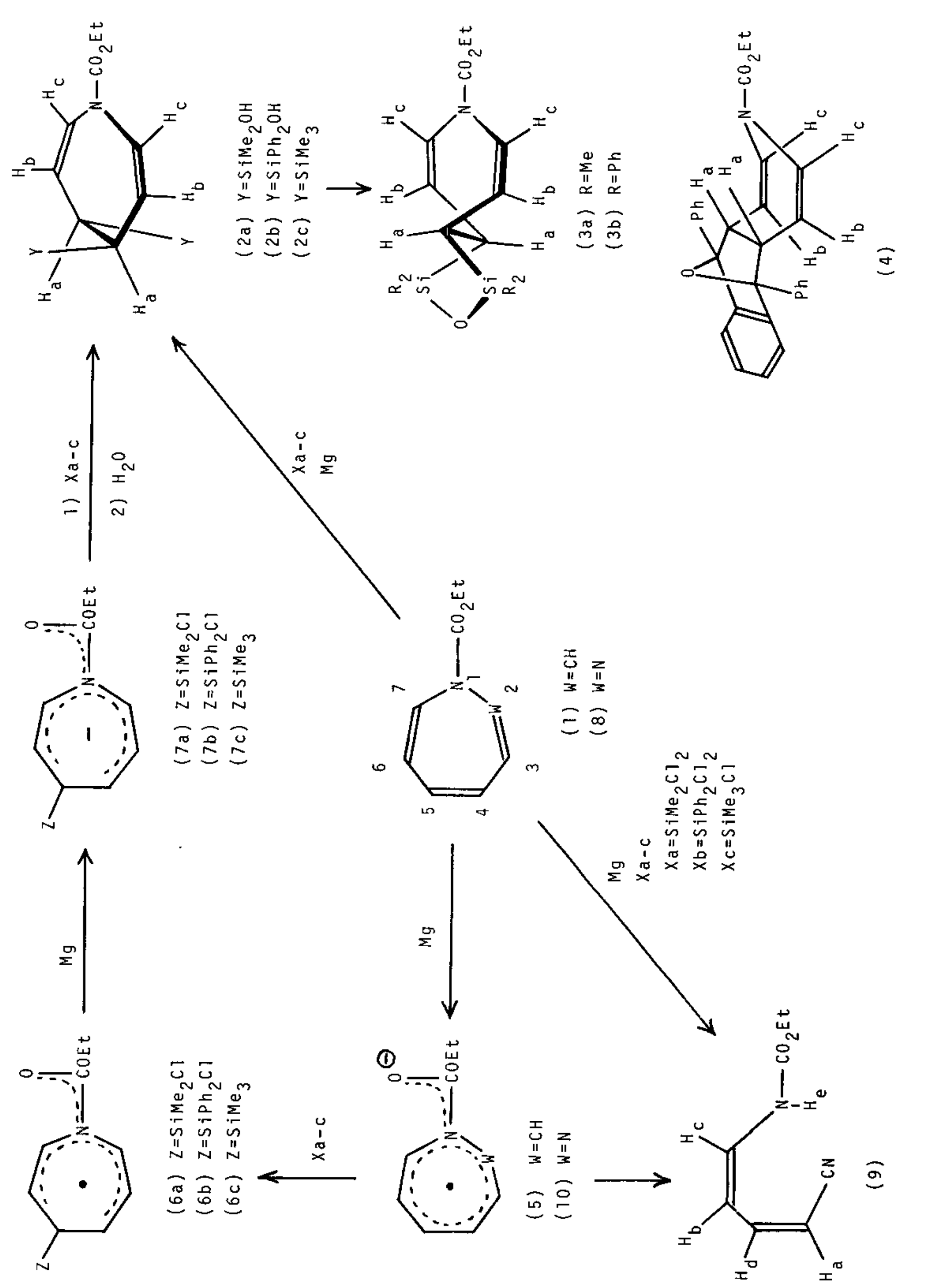
2b; UV (EtOH): 244 nm (sh. log ε, 4.4), 248 (4.4), 254 (4.3), 260 (4.2), 265 (4.0), 271 (3.9); IR (oil): 3420, 1710 cm^{-1}.

2c; UV (EtOH): 240 nm (log ε, 4.2); IR (oil): 1730 cm^{-1}.

3a; UV (EtOH): 238 nm (log ε, 4.2); IR (oil): 1730 cm^{-1}.

3b; UV (EtOH): 244 nm (sh. log ε, 4.3), 254 (4.2), 260 (4.1), 265 (4.0), 272 (3.8); IR (KBr): 1720 cm^{-1}.

The structures of 2 and 3 were deduced to be 4,5-adducts (trans-4,5-disubstituted-4,5-dihydroazepine derivatives) from the following spectral properties.



(2a) Y=SiMe$_2$OH
(2b) Y=SiPh$_2$OH
(2c) Y=SiMe$_3$
(3a) R=Me
(3b) R=Ph
(4)
1) Xa-c
2) H_2O
Xa-c
Mg
(7a) Z=SiMe$_2$Cl
(7b) Z=SiPh$_2$Cl
(7c) Z=SiMe$_3$
(1) W=CH
(8) W=N
Xa=SiMe$_2$Cl$_2$
Xb=SiPh$_2$Cl$_2$
Xc=SiMe$_3$Cl
(6a) Z=SiMe$_2$Cl
(6b) Z=SiPh$_2$Cl
(6c) Z=SiMe$_3$
(5) W=CH
(10) W=N
(9)

The fact that the NMR spectra of **2** and **3** contain three peaks (H_a, H_b, and H_c) each of which corresponds to two ring protons suggests that **2** and **3** are symmetric compounds (4,5-adducts or 2,7-adducts), and not unsymmetric compounds (2,3-adducts or 2,5-adducts). In the NMR spectra of **2** and **3** at low temperature (-30 ~ -50°C), the doublet peak of H_c split into two doublet peaks at slightly different chemical shifts, and the same phenomenon is observed with the authentic sample (**4**).[5] These properties are explained by considering that the two H_c protons are influenced by the different shielding effects of the ethoxycarbonyl group whose conformation is fixed at this low temperature.[6] This fact suggests that the two olefinic protons (H_c) are located near the nitrogen atom, and that the adducts are 4,5-adducts and not 2,7-adducts. In addition to this finding, the similarity of the NMR spectrum of **3** to that of **4** supports the substitution positions of the silyl groups as shown in the figure.

The trans-configuration of the silyl groups is deduced from the coupling constants in the NMR spectra. If the silyl groups of the silanols **2** are in trans-configuration, they should be arranged in axial positions because of their steric repulsion, and it follows that the angle between the equatrial H_a and the olefinic H_b should be about 10° judging from the Dreiding models. This is well coincident with the angle suggested by the coupling constants (J_{ab}, about 10 Hz) between these two protons.[7] On the other hand, the J_{ab} of **3** is about 2 Hz, almost equal to that of **4**. This is interpreted by considering that the arrangements of the silyl groups in **3** are equatrials because of their siloxane bond formation, and consequently that the angle between the axial H_a and olefinic H_b is about 100°, almost equal to that of 4.

The formation mechanism of the silanols **2** can be considered as follows. An electron transfer from magnesium to the azepine (**1**) forms the anion radical (**5**), which reacts with chlorosilanes to give the radical (**6**), and then, **6** accepts another electron from magnesium to produce the anion (**7**).[8] Reaction of another chlorosilane with **7** and subsequent hydrolysis of the resulting adduct gave the silanols **2**. The formation of the siloxanes **3** from **2** is not surprising because silanols are well known to be apt to form siloxanes upon heating.[9]

The addition reactions of 1-ethoxycarbonyl-1H-1,2-diazepine (**8**) with chlorosilanes (Xa-c) under the same conditions as above gave no adduct except almost 25 % yield of nitryl compound (**9**). The structure of **9** was deduced to be all-*cis*, mainly from the good coincidence of the coupling constants in its NMR spectrum with those of the corresponding all-*cis* nitryl compounds obtained by Streith et al.,[10] as well as the following spectral properties.

9; UV (EtOH): 303 nm (logε, 4.4); IR (KBr): 3330, 2210, 1710 cm^{-1}; NMR ($CDCl_3$) δ ppm: 1.3 (t, 3H), 4.3 (q, 2H), 5.09 (d, H_a), 5.23 (q, H_b), 6.86 (t, H_c), 7.09 (t, H_d), 7.75 (broad, H_e). Coupling constants (Hz), J_{ad}=10, J_{bc}=9, J_{bd}=12, J_{ce}=12.

The nitryl compound (**9**) is considered to be formed by N-N bond fission of the radical anion (**10**), because **9** is also formed by the reaction of **8** with magnesium in HMPA, and because diazepines are known to produce the nitryl compounds like **9** in the reactions with strong bases.[10]

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