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}.

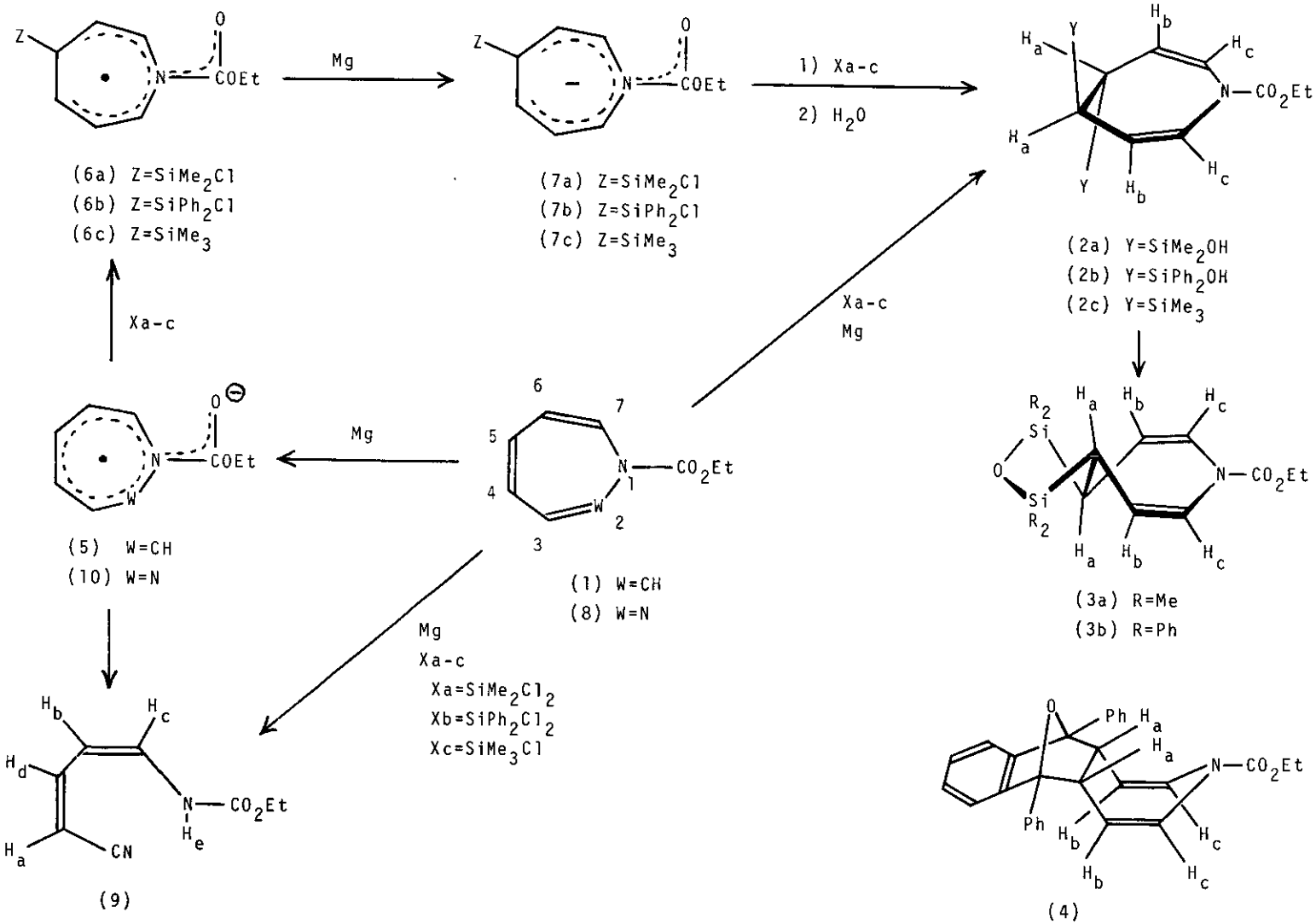
2b; UV (EtOH): 244 nm (sh. log ε, 4.4), 248 (4.4), 254 (4.3), 260 (4.2), 265 (4.0), 271 (3.9); IR (oil): 3420, 1710 cm^{-1}.

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.


Mg
1) Xa-c
2) H_2O
(6a) Z=$SiMe_2Cl$
(6b) Z=$SiPh_2Cl$
(6c) Z=$SiMe_3$
(7a) Z=$SiMe_2Cl$
(7b) Z=$SiPh_2Cl$
(7c) Z=$SiMe_3$
(2a) Y=$SiMe_2OH$
(2b) Y=$SiPh_2OH$
(2c) Y=$SiMe_3$
Xa-c
Mg
Xa-c
(5) W=CH
(10) W=N
Mg
(1) W=CH
(8) W=N
(3a) R=Me
(3b) R=Ph
Mg
Xa-c
Xa=$SiMe_2Cl_2$
Xb=$SiPh_2Cl_2$
Xc=$SiMe_3Cl$
(9)
(4)

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 (log ε, 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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