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Preliminary communication

Organosilicon heterocycles from ring expansion reactions

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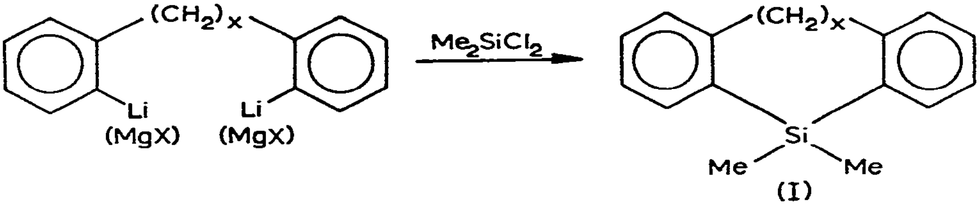
A standard approach to the synthesis of organosilicon heterocycles involves the reaction of an appropriate diGrignard or dilithio reagent with an organosilicon halide[1] (Eqn. 1). The diGrignard (dilithio) route is useful when a "symmetrical" heterocycle is desired, *i.e.*, a ring system that contains a plane of symmetry that bisects the molecule and contains the heteroatom.



(1)

(I)
x = 0, (Ia)[2]
x = 1, (Ib)[3]
x = 2, (Ic)[4]

Synthesis of isomers of the tricyclic heterocycles depicted by (Ib–Ic) would require Grignard reagents produced from organic bromides such as o-$BrC_6H_4C_6H_4CH_2Br$-o and o-$BrC_6H_4CH_2C_6H_4CH_2Br$-o. An alternative route to the synthesis of "unsymmetrical" tricyclic heterocycles (lacking a plane of symmetry) is suggested from the observation that $Ar_2Si(CH_2Ar)X$ is produced from Ar_3SiCH_2X by migration of an aryl group from silicon to carbon in the presence of a Lewis acid[5]. If this rearrangement is incorporated into a heterocyclic system, the result is expansion of the ring size. Ring expansion reactions have been reported for silicon monocycles[6].

The previously unreported heterocycles, (IIa–IIc) (Eqn. 2), necessary for the study of the ring expansion reaction have been prepared by the reaction of appropriate

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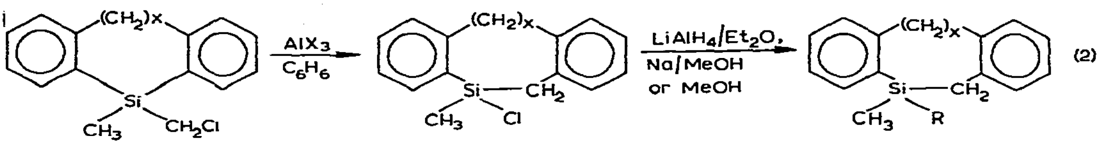


x = 0, (IIa)
x = 1, (IIb)
x = 2, (IIc)

x = 0, (IIIa)
x = 1, (IIIb)
x = 2, (IIIc)

diGrignard or dilithio reagents with $CH_3(CH_2Cl)SiCl_2$ (Eqn. 1). Compounds (IIa–IIc) were produced in yields of 40, 13.5 and 46%, respectively.

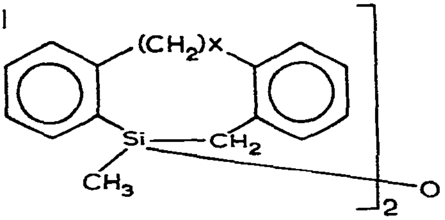
The ring expansion reaction was carried out in oven-dried glassware in a drybox under a nitrogen atmosphere. $AlCl_3$ or $AlBr_3$ was added to a solution of 0.5 to 1.0 g of (II) in 30 ml of anhydrous benzene and stirred for approximately 2 h after which the reaction was quenched by addition of $LiAlH_4$ in diethyl ether, methanol, Na in methanol, or water. Product mixtures were eluted over silica gel. Typical results are shown in Table 1. Chemical analyses and spectroscopic properties are consistent with the indicated product assignments. The *m/e* values obtained for the molecular ions for reactants (II) and products (III and IV)

TABLE 1

ORGANOSILICON HETEROCYCLES PREPARED BY RING EXPANSION

Reactant	*Catalyst*	*Time (h)*	*Work-up*	*Isolated product (%)*			*M.p. (°C)*
						R	
IIa ($x = 0$)	$AlBr_3$	2	Na/MeOH	IVa	48	–	115–117°
	$AlBr_3$	1	MeOH	IIIa	43	OMe, OH[a]	oil
IIb ($x = 1$)	$AlCl_3$	1¼	$LiAlH_4$	IIIb	53	H	oil
	$AlBr_3$	2¾	Na/MeOH	IVb	40	–	oil
IIc ($x = 2$)	$AlCl_3$	2	$LiAlH_4$	IIIc	60	H	oil
	$AlBr_3$	1	H_2O	IIIc	37	OH	80–82°
				IVc	10	–	143–145°
	$AlBr_3$	3½	MeOH	IVc	47	–	143–145°

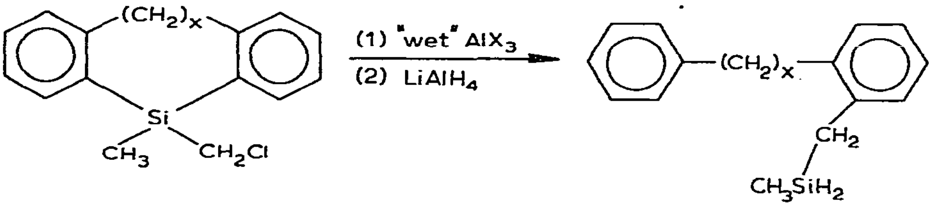
[a] Mixture



x = 0, (IVa)
x = 1, (IVb)
x = 2, (IVc)

are consistent with the calculated molecular weight for the monomer. The heterocyclic silanes (IIIb and IIIc) exhibited characteristic ν(SiH) and the siloxanes (IVa–IVc) characteristic ν(Si–O–Si) in the infrared spectra. The NMR data for the product ring systems exhibited Ar, $-Si-CH_2-$, and $-(CH_2)_x-$ absorptions with integrated intensities that agree with the reported products.

Prolonged exposure to the aluminum halide catalyst or trace amounts of moisture produce products of ring cleavage (Eqn. 3).



(3)

The dibenzheterocycles of structural types (II), (III) and (IV) have not been reported previously. The 5,6,11,12-tetrahydro-5*H*-dibenz[*b,f*] silicon, (IIIc), is the first dibenzheterocycle with a central eight-membered ring containing a single silicon heteroatom. In an attempt to generate benzsilacyclobutane, the dimer product, 2:3,6:7-dibenz-1,1,5,5-tetraphenyl-1,5-disila-2,6-cyclooctadiene was isolated in low yields from reaction of *o*-chlorobenzyldiphenylsilane with sodium[7]. A silaphenanthrene derivative has apparently been obtained but synthetic details have not been published[8].

The chemistry and structural features of these new heterocyclic compounds are currently under investigation and will be reported at a later date.

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