SYNTHESIS OF THE FIRST EXAMPLES OF 1-BENZOSILEPINE, 1-BENZOGERMEPINE, AND 1-BENZARSEPINE RING SYSTEMS

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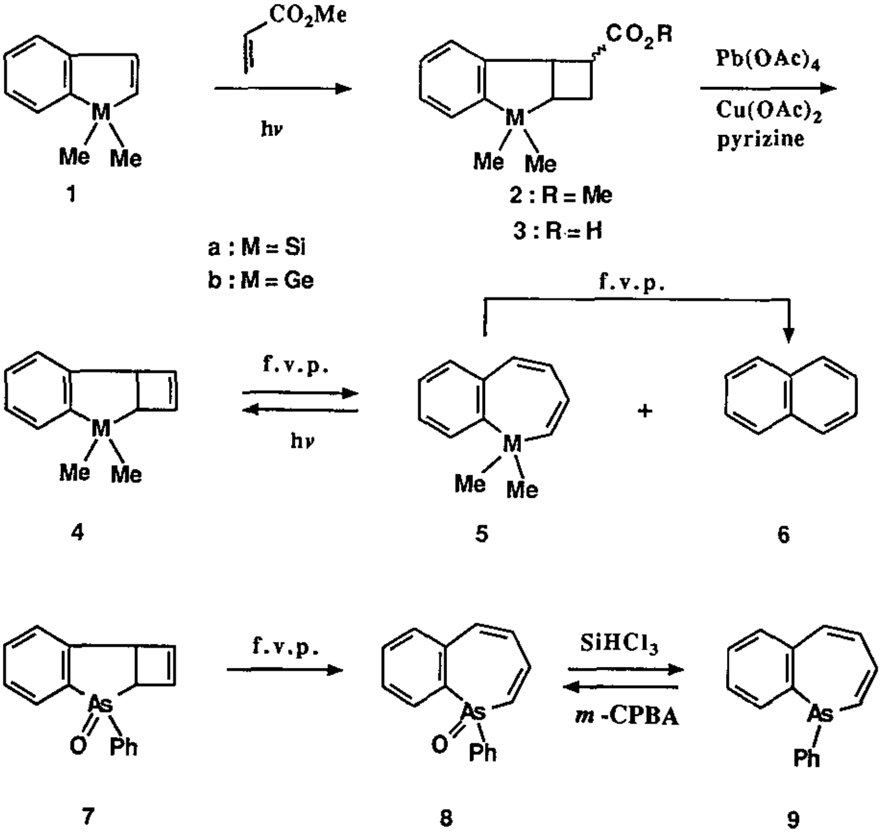
Abstract - The first synthesis of 1,1-dimethy-1-benzosilepine, 1,1-dimethy-1-benzogermepine, and 1-phenyl-1-benzarsepines was achived by flash vacuum pyrolysis of the dihydrocyclobut[*b*]benzoheteroles (**4**,**7**), prepared from the corresponding 1-benzoheteroles via three steps.

There has been considerable current interest in the synthesis of fully unsaturated seven-membered heterocyclic rings (heteroepines) containing an element other than nitrogen, oxygen, or sulfur and a variety of monocyclic and fused heteroepines have been prepared. With regard to benzoheteroepines, 3-benzoheteroepines containing B,[1] Si,[2] Sn,[3] P,[4] Sb,[5] or Te[6] are known, however, such 1-benzoheteroepines were not reported prior to several years ago. Therefore, we were interested in the synthesis of 1-benzoheteroepines containing Group 14, 15, and 16 heavier elements and have already reported the syntheses of 1-benzophosphepines,[7] 1-benzoselenepines[8] and 1-benzotellurepines.[8] We report here on the synthesis of the title 1-benzoheteroepines.

The 1-benzosilole (**1a**)[9] and 1-benzogermole (**1b**)[10] were irradiated with methyl acrylate to give the adducts (**2**), which were obtained as mixtures of two stereoisomers, but used in the following reactions without separation. The adducts (**2**) were hydrolysed and then oxidatively decarboxylated by treatment with lead tetraacetate in the presence of cupric acetate and pyridine giving rise to the starting tricyclic compounds (**4**)[11] in *ca.* 20% yields from **1**, via the acids (**3**). Although when the tricyclic compounds (**4**) were heated in diphenyl ether at 180 °C for 20 h, no reaction occurred. However, flash vacuum pyrolysis (f.v.p.) of **4** resulted in valence isomerization with ring opening to give the desired 1-benzosilepine (**5a**) and 1-benzogermepine (**5b**),[12] along with naphthalene, in the yields shown in Table 1. The heteroepines (**5**) easily reverted back to the starting tricyclic compounds (**4**) in high yields on irradiation in benzene.

Next, f.v.p. of the dihydrocyclobut[*b*]arsindole oxide (**7**),[11] prepared from 1-phenylarsindole[10] by similar procedures, also afforded the 1-benzarsepine 1-oxide (**8**)[12] and naphthalene in the yields shown in Table 1. Treatment of **8** with trichlorosilane gave the deoxygenated arsepine (**9**:75% yield), which reverted to the oxide (**8**) on treatment with m-chloroperbenzoic acid (*m*-CPBA) in 80% yield.



Scheme 1

Table 1 F. V. P. of **4** and **7**

Compd.	Temp. (°C)	Press. (Torr)	Yield (%)		
			5 or **8**	**6**	Recovery
4a	450	1.9×10^{-5}	59	tarce	40
	500	1.9×10^{-5}	84	12	2
	550	3.0×10^{-5}	77	21	...
4b	450	5.5×10^{-5}	33	15	50
	500	4.1×10^{-5}	47	42	10
	550	5.8×10^{-5}	15	83	...
7	500	1.7×10^{-5}	40	31	22
	530	2.2×10^{-5}	39	42	8
	550	1.1×10^{-5}	27	49	...

Both 1- and 3-benzoheteroepines containing heavier elements (S,[13] Se,[8] Te,[8] P[4,7]) are know to be thermolabile and gradually decomposed to naphthalene by extrusion of the hetero elements. However, the silepine (**5a**), germepine (**5b**) and arsepine oxide (**8**) are thermally stable and remained largely unchanged even when heated in solvents at 200 °C for 24 h, and undergo thermal decomposition to naphthalene only by further f.v.p. at 500-550 °C. The results shown in Table 1 indicate that the silepine (**5a**) is somewhat less thermolabile than the other heteroepines (**5b**) and (**8**). In contrast to the oxide (**8**), the deoxygenated arsepine (**9**) is extremely thermolabile and gradually decomposed even at room temperature. The half-life of **9** estimated by the ^{1}H-nmr spectral analysis in toluene at 80 °C is about 10 min. This thermal behaviour is similar to those of 1-phenyl-1-benzophosphepine ($t_{1/2}$ = 90 min at 80 °C),[7] 3-phenyl-3-benzophosphepine ($t_{1/2}$ = 120 min at 80 °C),[4] and 1-benzothiepine ($t_{1/2}$ = 58 min at 47 °C),[13] whose oxides are also thermally stable. Therefore, the oxide group in **7** is essential for the present thermal isomerization to benzarsepines, in fact, f.v.p. of the dihydrocyclobut[*b*]arsindole having no oxide group gave only naphthalene, derived from the initially formed benzarespine (**9**).

Further studies on the reactions of these new heterocyclic ring systems are in progress.

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11. Satisfactory elemental analyses and spectral data were obtained for all new compounds reported. **4a**: Oil, bp_{25} 112-113 °C; ^{1}H-nmr ($CDCl_3$) δ 0.33 and 0.40 (each 3H, s), 2.84 (1H, d, J=3.7 Hz), 4.52 (1H, d, J=3.7 Hz), 6.29 (2H, s); **4b**: oil; 7: mp 196-198 °C.
12. **5a**: Oil; ^{1}H-nmr ($CDCl_3$) δ 0.29 (6H, s, $SiMe_2$), 5.88 (1H, d, 2-H), 6.30 (1H, dd, 4-H), 6.79 (1H, dd, 3-H), 6.91 (1H, d, 5-H), $J_{2,3}$= 14.3, $J_{3,4}$= 5.9, $J_{4,5}$= 13.2 Hz: **5b**: oil; 1H-nmr δ 0.38 (6H, s, $GeMe_2$), 5.97 (1H, d, 2-H), 6.26 (1H, dd, 4-H), 6.71 (1H, dd, 3-H), 6.81 (1H, d, 5-H), $J_{2,3}$= 13.2, $J_{3,4}$= 5.8, $J_{4,5}$= 13.2 Hz; **8**: mp 158-159 °C; **9**: oil, ^{1}H-nmr δ 6.17 (1H, d, 2-H), 6.46 (1H, dd, 4-H), 6.66 (1H,dd, 3-H), 7.02 (1H, d, 5-H), $J_{2,3}$= 11.3, $J_{3,4}$= 5.3, $J_{4,5}$= 12.5 Hz. Very recently, we have found a different synthetic route to the 1-benzoarsepine (**9**) from (Z)-*o*, β-dibromostyrene *via* five steps.
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