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SYNTHESIS AND REACTIVITY OF SOME *N*-TRIPHENYLGERMYL HETEROCYCLIC AMINES

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Summary

Five new *N*-triphenylgermyl heterocyclic amines have been prepared: the imidazole, phthalimide, succinimide, pyrazole, and 1,2,4-triazole derivatives, as well as the previously reported *N*-triphenylgermylpyrrole. The reactivity of these compounds toward a series of nucleophilic reagents has been determined and compared with the reactivity of an analogous series of *N*-tributylgermyl compounds. The greater reactivity of the *N*-triphenylgermyl compounds rules out any possibility of stabilization of the Ge—N bond by through conjugation between the π-systems of the phenyl groups and the heterocyclic amine.

Introduction

Organogermanium compounds containing Ge—N bonds have been extensively described in the literature [1]. For the most part those compounds which have been prepared have been alkyl derivatives; comparatively few triphenylgermyl-nitrogen compounds have been described; exceptions are $(Ph_3Ge)_2NH$ [2], Ph_3GeNPh_2 [3], and $Ph_3GeNC_4H_4$ (NC_4H_4 = pyrrole) [4]. Compounds of this type, particularly those such as the pyrrole derivative, are of interest because they would allow a test of the possibility of "through-conjugation", interaction through the *d* orbitals of germanium between the π-systems of the phenyl and heterocyclic rings.

Rijkens, Janssen and Van der Kerk [4] have investigated the stability of the Ge—N bond toward nucleophilic attack in a series of *N*-tributylgermyl compounds in which the nitrogen atom is part of a heterocyclic ring. The pyrrole, pyrrolidine, pyrazole, imidazole, indole, and triazole derivatives were prepared and their reactivity toward various nucleophilic reagents determined. They also prepared one *N*-triphenylgermyl derivative, *N*-triphenylgermylpyrrole, and reported that it was remarkably stable; it could be dissolved in acetone and reprecipitated by water without decomposition. Such a result would be expected if stabilization of the Ge—N bond by through-conjugation between π-systems were possible. In order to further test this hypothesis, we prepared a series of *N*-triphenylgermylnitrogen compounds analogous to the *N*-tributylgermyl compounds prepared by Rijkens et al., and compared their stability toward nucleophilic attack under the same conditions.

Experimental

Chemicals and reagents. Germanium tetrachloride was obtained from Sylvania Electric Products and used without further purification. From it, tetraphenylgermane [5], triphenylbromogermane [6], and hexaphenyldigermoxane [7] were prepared by methods described in the literature. Succinimide was prepared by the method reported by Clarke and Behr [8]. All of the other heterocyclic amines were obtained from Aldrich Chemical Company and used without further purification.

All reactions were run under an atmosphere of dry nitrogen and care was taken to exclude moisture. All glassware was dried at 125°C. Solvents were purged of oxygen by bubbling dry nitrogen through the solvent for several minutes. Work up of reaction products and preparation of samples for infrared or elemental analysis were carried out in a LABCONCO Controlled Atmosphere glove box using an atmosphere of dry nitrogen.

Infrared spectra were obtained using a Beckman IR 4240 spectrophotometer. Solid samples were run as mulls in Nujol using Crystal Lab KBr Plates. Liquid samples were run using 0.1 mm Beckman KBr sealed cells.

Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of N-triphenylgermylimidazole. *N*-Triphenylgermylimidazole was prepared by two methods. 1. A mixture of hexaphenyldigermoxane (6.24 g, 0.01 mol) and imidazole (1.36 g, 0.02 mol) was placed in a 100 ml four neck round bottom flask fitted with a distilling trap. The mixture was heated to 170°C. Over a two hour period 50 ml of dry toluene was added and the reaction mixture kept at reflux for 24 hours. Heating was terminated and as soon as refluxing ceased the reaction vessel was sealed and transferred to the glove box. The reaction mixture was filtered while hot by suction; upon cooling, crystals of crude product separated. These were recrystallized from benzene yielding 1.5 g (20%) *N*-triphenylgermylimidazole, a crystalline white solid, m.p. 139—140°C. Analysis: C, 67.78; H, 4.88; Ge, 19.32; N, 7.59. $C_{21}H_{18}GeN_2$ calcd.: C, 67.98; H, 4.90; Ge, 19.57; N, 7.55%.

2. A solution of triphenylbromogermane (5.76 g, 0.015 mol) in 30 ml toluene was added dropwise to a suspension of potassium imidazole, prepared by refluxing a mixture of imidazole (1.23 g, 0.018 mol) and potassium (0.59 g, 0.015 mol) in 40 ml toluene for one hour. The reaction mixture was refluxed for two hours, then heating stopped and, upon cessation of reflux, the vessel was sealed and transferred to the glove box. The mixture was filtered while hot by suction. After evaporation of approximately 20 ml of the filtrate, crystals separated. These were collected and recrystallized from benzene, yielding 2.1 g (36%) *N*-triphenylgermylimidazole, m.p. 137—138°C.

Following the same procedure, and on the same scale, four other previously

TABLE 1

NEW *N*-TRIPHENYLGERMYL HETEROCYCLIC AMINES

Method of preparation: $Ph_3GeBr + KN \xrightarrow{\text{toluene}} Ph_3GeN + KBr$

N-Triphenylgermyl amine	Reflux time (h)	Physical state	M.p. (°C)	Yield (%)	Analysis: Found (calcd.) (%)			
					C	H	Ge	N
1,3-Diazole (imidazole)	2	White crystals	139—140	36	67.78 (67.98)	4.88 (4.90)	19.32 (19.57)	7.59 (7.55)
1,2-Diazole (pyrazole)	6	White crystals	147—148	30	68.46 (67.98)	5.20 (4.90)	19.98 (19.57)	6.27 (7.55)
1,2,4-Triazole	3	White crystals	158—159	31	64.80 (64.57)	4.77 (4.62)	19.59 (19.51)	9.25 (11.30)
Phthalimide	2	Pale green crystals	169—170	23	69.51 (69.38)	4.37 (4.26)	16.37 (16.13)	3.18 (3.11)
Succinimide	2	White crystals	142—143	26	64.45 (64.67)	4.85 (4.92)	18.69 (18.61)	3.40 (3.59)

unreported compounds were also prepared from triphenylbromogermane and the potassium salt of an amine. Reflux times, yields, physical properties, and elemental analyses of the compounds prepared by this procedure are shown in Table 1.

Preparation of N-triphenylgermylpyrrole. Following a procedure similar to that reported by Rijkens et al. [4], *N*-triphenylgermylpyrrole was prepared by placing pyrrole (1.34 g, 0.02 mol) and sodium (0.46 g, 0.02 mol) in 40 ml toluene in a 100 ml three neck flask and refluxing for one hour. To the blue suspension resulting was added a solution of triphenylbromogermane (10 g, 0.026 mol) in 30 ml toluene. The reaction mixture was allowed to reflux overnight, then the vessel was sealed and transferred to the glove box. The reaction mixture was filtered while hot by suction. Upon cooling to room temperature, white crystals separated. These were collected and recrystallized from benzene, yielding 4.9 g (50%) *N*-triphenylgermylpyrrole, m.p. 198—199°C (Lit. [4] 198—199°C).

Reactivity experiments. A study of the reactivity of the compounds prepared was carried out by mixing the compounds with various nucleophiles, placing the mixtures into liquid cells, and observing the infrared spectrum over a period of time.

Solutions 0.05 *M* in the compounds were prepared in benzene and the infrared spectrum obtained. The nucleophile was then added in equimolar concentration and further spectra were obtained until a reaction was observed or until five days had lapsed and no detectable change had occurred.

Results and discussion

Identification of the previously unreported compounds was primarily from agreement of the elemental analysis and infrared spectra with those expected.

Earlier attempts in this laboratory to prepare these compounds [9] had lead to the conclusion that it would be even more difficult to obtain pure compounds free from the products of hydrolysis and/or air oxidation than had been reported for the *N*-tributylgermyl derivatives. Consequently all synthetic procedures were carried out under an atmosphere of nitrogen with care taken to exclude all moisture. Work up of reaction mixtures and the preparation of samples for infrared and elemental analysis, as well as for the reactivity experiments were carried out under an atmosphere of dry nitrogen in a glove box.

Even so, the infrared spectra of the phthalimide, imidazole, and triazole derivatives show bands at 860 cm^{-1} characteristic of organogermanium oxides [10]. Elemental analyses of the pyrazole and triazole compounds show low percentages of nitrogen and high percentages of germanium, consistent with the presence of some hexaphenyldigermoxane, $[(C_6H_5)_3Ge]_2O$, impurity. A mixture of 95% *N*-triphenylgermyl-1,2,4-triazole with 5% hexaphenyldigermoxane would have C, 64.83; H, 4.61; Ge, 19.70; N, 10.73%, as compared with experimental C, 64.80; H, 4.77; Ge, 19.59; N, 9.25%. From the elemental analysis the pyrazole derivative could contain up to 17% oxide; a mixture of 83% *N*-triphenylgermylpyrazole and 17% hexaphenyldigermoxane would give C, 68.22; H, 4.87; Ge, 20.20; N, 6.27%. The experimental values are C, 68.46; H, 5.20; Ge, 19.98; N, 6.27%. However the infrared spectrum does not indicate the oxide to be present to this extent in the latter compound. Either further reaction occurred during preparation of the sample for nitrogen analysis or that analysis was low for some other reason.

Preparation of several other *N*-triphenylgermyl heterocyclic amines was attempted. These were the pyrrolidine, 2,5-dimethylpyrrole, and indole derivatives. The preparative methods attempted were similar to those reported in the literature [4,11] for other organogermanium nitrogen compounds. The attempted preparation of the indole and 2,5-dimethylpyrrole derivatives from triphenylbromogermane and potassium amines followed the same procedure as that described for the preparation of *N*-triphenylgermylimidazole (method 2). In the first case, unreacted triphenylbromogermane was recovered from the reaction mixture; in the second the only product isolated was hexaphenyldigermoxane. The attempted preparation of triphenylgermylpyrolidine from triphenylgermyllithium and *N*-chloropyrrolidine gave triphenylchlorogermane as the only product isolated. Earlier attempts in this laboratory to prepare these compounds have also been unsuccessful [9].

Reactivity experiments

A series of experiments were conducted to determine the reactivity with nucleophilic reagents of the compounds prepared. The results are tabulated in Table 2. The procedure for carrying out these experiments was the same as that used by Rijkens, Janssen and Van der Kerk [4] for the *N*-tributylgermyl analogs. The progress of the reactions was followed qualitatively by monitoring changes in the IR spectrum of solutions containing both the organogermanium nitrogen compound and a nucleophile after mixing as compared with spectra of the solutions separately before mixing. Since the triphenylgermyl derivatives were less soluble in benzene than the tributylgermyl compounds, solutions were 0.05 molar in these reagents rather than 0.5 molar as in the earlier work. This increased the difficulty of detecting changes in absorption over the benzene background, but not so much as to preclude use of this method.

In general, the results of these reactivity experiments closely parallel those

TABLE 2

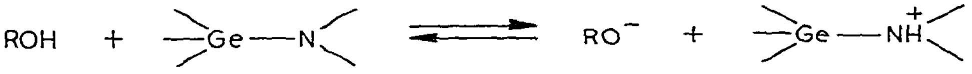
REACTIVITY OF *N*-TRIPHENYLGERMYL HETEROCYCLES

N-Triphenylgermyl heterocycles	Nucleophiles [a]				
	Phenol	Ethanol	t-Butanol	Phenyl-acetylene	Octylamine
1,2,4-Triazole	R-1	R-1	NR	NR	R-2
1,2-Diazole (pyrazole)	R-1	R-1	NR	NR	R-1
1,3-Diazole (imidazole)	R-1	R-1	NR	NR	R-1
Phthalimide	NR	NR	NR	NR	NR
Succinimide	R-2	NR	NR	NR	NR
Pyrrole	NR	NR	NR	NR	NR

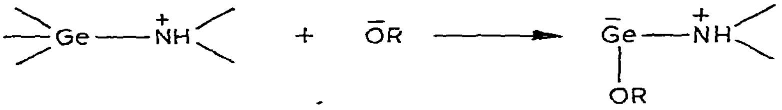
[a] R-1 = reaction complete during time taken to prepare IR samples. R-2 = reaction complete after approximately 12 hours. NR = stable for at least five days.

found in the earlier study of the tributylgermyl compounds. Amines having more than one ring nitrogen (pyrazole, imidazole, 1,2,4-triazole) were more susceptable to nucleophilic attack than those containing one nitrogen (phtalimide, succinimide, pyrrole). The order of reactivity of the nucleophiles found in the earlier study (phenol > ethyl alcohol > t-butyl alcohol > phenylacetylene > octylamine) was also reflected in our results. The only important difference is that the *N*-triphenylgermyl-imidazole, -triazole, and -pyrazole derivatives reacted with octylamine whereas the corresponding *N*-tributylgermyl derivatives did not.

Since the order of reactivity of the nucleophiles reflected the acid strength of the reagents rather than the order of increasing nucleophilicity, Rijkens, Janssen and Van der Kerk proposed a reaction mechanism in which electrophilic attack at nitrogen (eq. 1—2) precedes nucleophilic attack at germanium (eq. 3), or in which both occur in a concerted mechanism involving a four-centered transition state:



(1)



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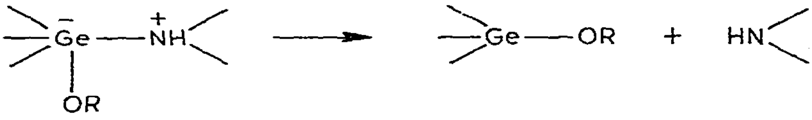

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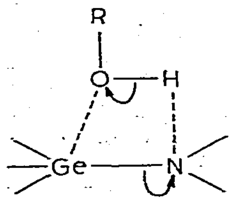

If ($p \rightarrow d \rightarrow \pi$) through conjugation were taking place the *N*-triphenylgermyl heterocyclic amines should be more stable, or less reactive, than the *N*-tributylgermyl analogs. This should be the case whether the determining factor in such stability were thermodynamic or kinetic. If thermodynamic, increased aromatic character and electron delocalization should stabilize the triphenylgermyl compounds more than the tributylgermyl compounds relative to possible products of the reaction. If kinetic, strengthening the Ge—N bond should increase the activation energy of any rate-determining step involving attack at that bond, whether nucleophilic attack at germanium or electrophilic attack at nitrogen.

Recently, an electron-spin resonance study [12] of the radical anions of di-4-biphenyldimethylsilane and related compounds has cast considerable doubt on the possibility of through conjugation between aromatic systems bridged by the $SiMe_2$ group. The possibility of "competitive π-bonding" by which the presence of several π-donor groups attached to a central atom leads to a decrease in the amount of π-bonding per substitution, might also be considered. Existing experimental evidence for such an effect in Group IVB compounds is hardly compelling, and there are theoretical arguments against it being likely [13], but the possibility has been raised to explain trends in the bond energies [14] and NMR chemical shifts [15] of organosilicon compounds. Such competitive π-bonding would lead to lessened stability of the Ge—N bond in triphenylgermyl derivatives relative to the trialkylgermanes.

Our results indicate that the triphenylgermyl derivatives were at least as reactive toward the nucleophiles studied as their tributylgermyl analogs. Considering the greater difficulty in the synthesis of these compounds, and the greater reactivity of three of them toward octylamine, it must be concluded that the triphenylgermyl heterocyclic amines are, if anything, more reactive toward nucleophilic attack than the tributylgermyl compounds.

If ($p \rightarrow d \rightarrow \pi$) interaction occurs, it can only be such that it takes place to a greater extent in a transition state or reaction intermediate, than in the ground state. Such stabilization of an excited state would enhance reactivity. Alternatively, our results could be rationalized if competitive π-bonding rather than through conjugation were taking place in the phenyl derivatives.

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