



Pergamon

Tetrahedron Letters 41 (2000) 3153–3155

TETRAHEDRON
LETTERS

A new and convenient synthesis of germatranes using molecular sieves (3 Å) as dehydrating agents

Qingmin Wang and Runqiu Huang*

Research Institute of Elemento-Organic Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Received 8 November 1999; accepted 28 February 2000

Abstract

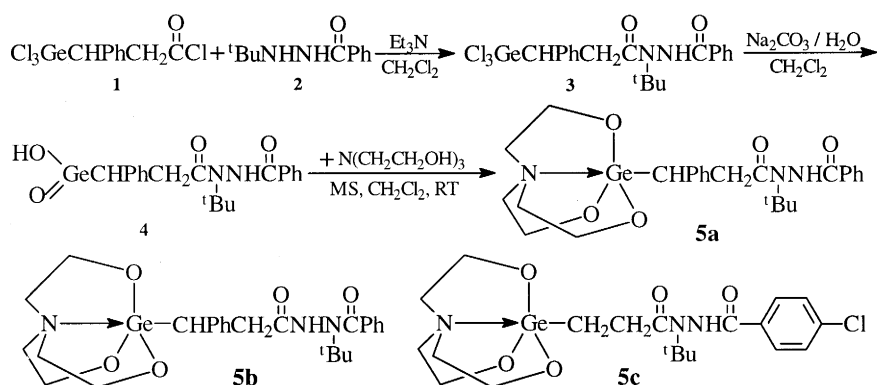
Germatranes were obtained by condensation reactions of germasesquioxides with triethanolamines using molecular sieves (3 Å) as dehydrating agents at room temperature in good yields. This new and highly efficient method for the synthesis of germatranes enjoys a number of advantages in that the reaction is carried out under mild conditions in good yields, starting materials are cheap or easily prepared, the experimental procedure is very simple and this method may be applicable to large scale production. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: germatranes; germasesquioxides; molecular sieves (3 Å).

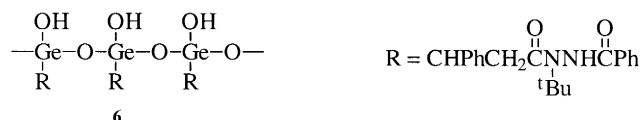
Germatranes as compounds with metalatrane skeletons have attracted considerable attention because of their unusual physical and chemical properties and marked biological activities.^{1–3} Three methods have usually been used for the synthesis of germatranes: (i) condensation of germasesquioxides with triethanolamines in toluene or ethanol at reflux temperature; (ii) interaction of trialkoxygermyl derivatives of organogermanic compounds with triethanolamines; and (iii) interaction of trialkoxygermyl or trichloro-germyl derivatives of organogermanic compounds with tris(trimethylsilyl) derivatives of triethanolamine.^{4–8} However, methods (i) and (ii) require rigid experimental conditions and provide lower yields (ca. 50–70%) and method (iii) has its limitations for the synthesis of germatranes owing to the difficulty of preparing tris(trimethylsilyl) derivative of triethanolamine as the starting material. Consequently, the development of a convenient method to obtain germatranes is still required. In this paper, we report a novel synthesis of germatranes by condensation of germasesquioxides with triethanolamines using molecular sieves (3 Å) as dehydrating agents at room temperature according to Scheme 1.

The key step of this procedure lies in the condensation of germasesquioxides with triethanolamines using molecular sieves (3 Å) as dehydrating agents. In this case, the condensation reaction is favored when germasesquioxides have good solubility in organic solvents. In previous work,^{9,10} we demonstrated that the pH of the solution may affect the degree of polymerization (D.P.) and the solubility of the

* Corresponding author. Tel: 0086-022-23502673; fax: 0086-022-23503438; e-mail: huangrq@sun.nankai.edu.cn (R. Huang)



germasesquioxides resulting from the hydrolysis of the organogermanium trichlorides. We found that the hydrolysis of **3**¹¹ was carried out with saturated sodium carbonate to give **4** which has the polymeric chain structure **6** as shown in Scheme 2. ¹H NMR, IR and elemental analysis data supported the structure of the compound **4**.¹² We demonstrated that **4** with the polymeric chain structure has good solubility in organic solvents such as methylene dichloride, chloroform, 1,2-dichloroethane and so on. Then compound **4** was condensed with triethanolamine using molecular sieves (3 Å) as dehydrating agents at room temperature to give the desired compound **5a** in 92% yield.¹³ The germatranes **5b** and **5c** were similarly prepared.



For comparison purposes, we also synthesized products **5a**, **5b** and **5c** by condensation of germasesquioxides with triethanolamines in toluene at reflux temperature (Table 1).

Table 1
Yields of products **5a**, **5b** and **5c**

Yields	5a	5b	5c
Reported Method i	75	75	72
New Method	92	92	92

In conclusion, this study has demonstrated that condensation of germasesquioxides with triethanolamines using molecular sieves (3 Å) as a dehydrating agent represents a highly efficient method for the synthesis of germatranes. Some advantageous features are: (a) the starting materials are cheap or easily prepared; (b) the experimental procedure is very simple; (c) the yield is very high; (d) this method may be applicable to large scale production.

Acknowledgements

We gratefully acknowledge support of this work by the National Natural Science Foundation of China.

References

- Gar, T. K.; Mironov, V. F. *Metalloorg. Khim.* **1988**, *1*, 260.
- Kakimoto, N.; Sato, K.; Matsui, M.; Takada, T.; Akiba, M. *Heterocycles* **1986**, *24*, 3047–3052.
- Zeng, Q.; Zeng, X. S.; Wang, Q. M.; Cui, T.; Xu, F. B. *Guangdong Weiliang Yuansu Kexue* **1998**, *5*, 5–15.
- Zhang, Z. B.; Li, L. S.; Chen, R. Y. *Heteroatom Chemistry* **1999**, *10*, 73–78.
- Mehrotra, R. C.; Chandra, G. *Indian J. Chem.* **1965**, *3*, 497.
- Gar, T. K.; Khromova, N. Yu.; Sonina, N. V.; Nikitin, V. S.; Polyakova, M. V.; Mironov, V. F. *Zh. Obshch. Khim.* **1979**, *49*, 1516.
- Kakimoto, N.; Sato, K.; Takada, T.; Akiba, M. *Heterocycles* **1985**, *23*, 1493.
- Lukevits, E. YA.; Germane, S. K.; Zidermane, A. A.; Dauvarte, A. Zh.; Kravchenko, I. M.; Trushule, M. A.; Mironov, V. F.; Gar, T. K.; Khromova, N. Yu.; Viktorov, N. A.; Shirzaev, V. I. *Khim. Farm. Zh.* **1984**, *18*, 154.
- Wang, Q. M.; Chen, Z.; Zeng, Q.; Huang, R. Q. *Heteroatom Chemistry* **1999**, *10*, 209–211.
- Zhang, Z. B.; Li, L. S.; Chen, R. Y.; Wang, Q. M.; Zeng, Q. *Chinese Chemical Letters*, **1997**, *8*, 9–10.
- Compound **3** was prepared from 3-phenyl-3-(trichlorogermanyl)propionyl chloride **1**^{11a-c} and *N'*-*t*-butyl-*N*-benzoylhydrazine **2**^{11d,e} in 83% yield. The structure of **3** was confirmed by ¹H NMR, IR and elemental analysis data. For the synthesis of **1** and **2**, see: (a) Zeng, Q.; Zeng, X. S.; Wang, Q. M.; Cui, T.; Zhang, Z. B. *Chin. J. Chem.* **1998**, *16*, 184–192. (b) Poskozim, P. S. *J. Organomet. Chem.* **1968**, *12*, 115–121. (c) Wang, Q. M.; Zeng, Q.; Chen, Z. *Heteroatom Chemistry* **1999**, *10*, 5–8. (d) Wang, Q. M.; Huang, R. Q. *Phosphorus, Sulfur, and Silicon and the Related Elements* in press. (e) Wing, K. D. US Patent 5 424 333 (1995). [*Chem. Abstr.* **123** (1995) 313108e]
- Compound **4**: To a solution of the compound **3** (2.5 mmol) in methylene dichloride (10 mL), a saturated solution of sodium carbonate was added with vigorous stirring. After the addition, the resulting mixture was stirred at room temperature for 12 h. The water phase was extracted three times with 20 mL of methylene dichloride. The extraction solvent was combined with the organic phase. The solvent was removed by distillation to give a white solid. The solid was then washed successively with distilled water and ether. Finally, a white powder **4** was obtained in 90% yield. ¹H NMR(CF₃CO₂D, 200MHz) δ: 1.46 (s, 9H, ¹Bu), 2.12 (m, 2H, CH₂CO), 3.12 (br., 1H, GeOH), 3.76 (m, 1H, CHGe), 7.04–7.86 (m, 10H, Ph); IR(KBr): 3393.0, 3053.5, 2916.0, 1665.4, 1608.7, 1579.8, 1518.2, 1481.4, 1450.8, 1389.3, 1362.3, 1272.7, 1235.4, 1210.4, 1185.0, 1069.1, 1023.0, 867.6, 804.3, 772.0, 692.6, 646.7, 459.3 cm⁻¹. Anal. calcd. for C₂₀H₂₄N₂O₄Ge C 55.99, H 5.63, N 6.52; found C 56.07, H 6.00, N 6.43.
- Compound **5a**: To a solution of compound **4** (1 mmol) and triethanolamine (1.2 mmol) in methylene dichloride (20 mL) was added molecular sieves (3 Å) (2 g) at room temperature. The reaction mixture was stirred for 20 h at room temperature. The solid was filtered off and the filtrate was concentrated under reduced pressure. A colorless crystalline solid that crystallized from the solution was dried under vacuum to give the desired compound **5a** in 92% yield. Mp 236–237°C (from CH₂Cl₂/petroleum ether (60–90°C)), ¹H NMR(CDCl₃, 200MHz) δ: 1.26 (s, 9H, ¹Bu), 2.35 (m, 2H, CH₂CO), 2.66 (m, 1H, CHGe), 2.73 (t, 6H, ³J_{HH}=5.4Hz, NCH₂), 3.67 (t, 6H, ³J_{HH}=5.4Hz, OCH₂), 7.00–7.30 (m, 10H, Ph), 8.04 (s, 1H, NH); IR(KBr): 3245.5, 3046.0, 2902.0, 1675.6, 1634.8, 1600.0, 1509.9, 1484.4, 1462.9, 1381.5, 1359.5, 1270.2, 1238.2, 1207.9, 1184.2, 1161.9, 1102.1, 1069.5, 1043.1, 1017.6, 926.1, 898.3, 794.6, 716.1, 688.8, 650.5, 580.5, 533.4 cm⁻¹. Anal. calcd for C₂₆H₃₅N₃O₅Ge C 57.59, H 6.50, N 7.75; found C 57.92, H 6.41, N 7.91.