The Crystal Structure of 1-(4-Ethoxy-Carbonylphenyl)Germatrane

Edmunds Lukevics*, Luba Ignatovich, Tatyana Shul'ga and Sergey Belyakov

Latvian Institute of Organic Synthesis, Aizkraukles 21, Riga, LV-1006, Latvia ign@osi.lv

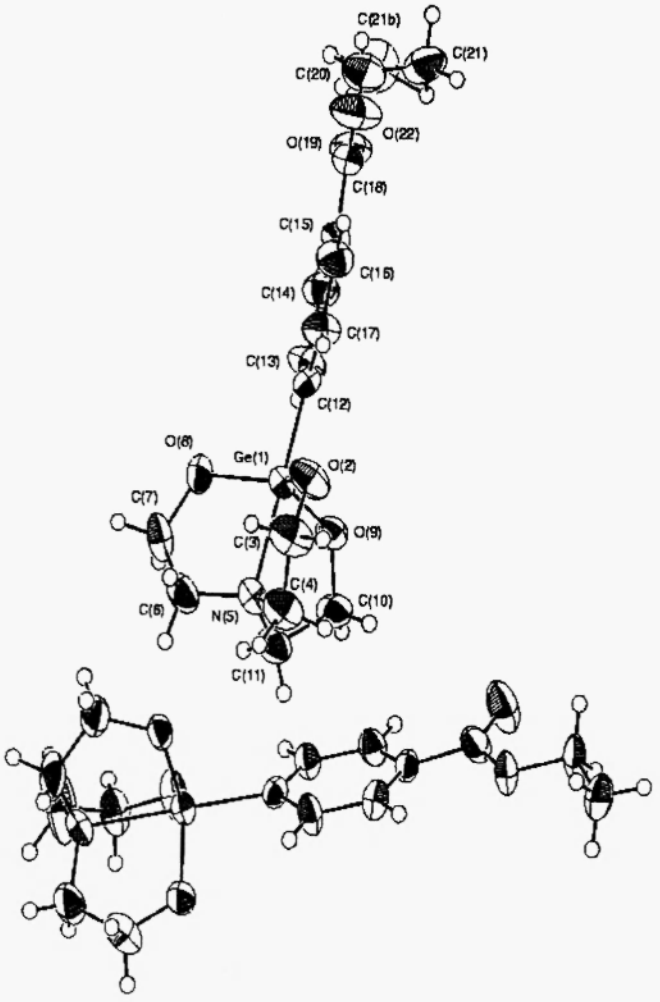
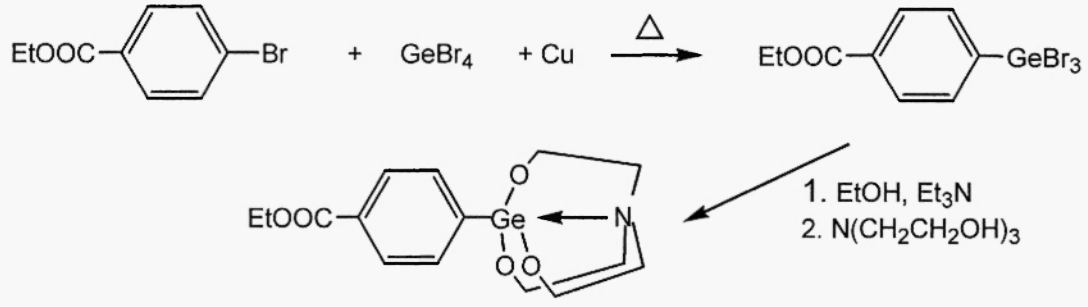


Figure 1. Molecular structure of 1-(4-ethoxycarbonylphenyl)germatrane. Selected geometric parameters: O(2)-Ge(1)-O(8) 122.2(2), O(2')-Ge(1')-O(8') 122.8(2), O(2)-Ge(1)-O(9) 116.4(2), O(2')-Ge(1')-O(9') 114.9(2), O(8)-Ge(1)-O(9) 116.2(2), O(8')-Ge(1')-O(9') 116.9(2), O(2)-Ge(1)-N(5) 82.77(15), O(2')-Ge(1')-N(5') 82.84(14), O(8)-Ge(1)-N(5) 82.4(2), O(8')-Ge(1')-N(5') 81.7(2), O(9)-Ge(1)-N(5) 82.24(14), O(9')-Ge(1')-N(5') 82.01(14), C(12)-Ge(1)-N(5) 178.7(2), C(12')-Ge(1')-N(5') 179.3(3), and C(13)-C(12)-Ge(1) 119.9(4) C(13')-C(12')-Ge(1') 119.8(3)°, Ge(1)-O(2) 1.781(3), Ge(1')-O(2') 1.801(3), Ge(1)-O(8) 1.816(3), Ge(1')-O(8') 1.791(3), Ge(1)-O(9) 1.813(3), Ge(1')-O(9') 1.791(3), Ge(1)-C(12) 1.961(5), Ge(1')-C(12') 1.968(4), O(2)-C(3) 1.440(6), O(2')-C(3') 1.407(6), O(8)-C(7) 1.403(6), O(8')-C(7') 1.392(6), O(9)-C(10) 1.396 (6), O(9')-C(10') 1.415 (6), C(4)-N(5) 1.441(6), C(4')-N(5') 1.468(7), C(6)-N(5) 1.483 (7), C(6')-N(5') 1.425(7), and C(11)-N(5) 1.477(7), C(11')-N(5') 1.414(7) Å.

COMMENT

We have synthesized a new representative of arylgermatranes – 1-(4-ethoxycarbonylphenyl)germatrane by reaction of ethyl 4-bromobenzoate and germanium tetrabromide in the presence of copper powder, conversion of 1-(4-ethoxycarbonylphenyl)tribromogermane to triethoxyderivative by alcoholysis, and subsequent transalkoxylation with triethanolamine to 1-(4-ethoxycarbonylphenyl)germatrane:



The X-ray crystal structure of 1-(4-ethoxycarbonylphenyl)germatrane (Figure 1) reveals that there are two symmetrically non-equivalent molecules (**A** and **B**), the germanium atom is pentacoordinated and adopts trigonal bipyramidal geometry. Three oxygen atoms are positioned in an equatorial fashion. The 4-ethoxycarbonylphenyl group and the nitrogen atom each occupy an apical position with transannular N→Ge bond of 2.211 (4) and 2.201(4) Å. The deviation of Ge atom (ΔGe) from the O(2) O(8) O(9) plane is 0.2381(9) and ΔGe' from O(2') O(8') O(9') plane is 0.2423(9) Å in the direction of the C(12) and C(12') atom. The transannular N→Ge bond in 1-(4-ethoxycarbonylphenyl)germatrane is comparable with that in other investigated 4-substituted phenyl-germatranes [1-3], but it is longer than that in the furan analogue (for 5-ethoxycarbonyl-2-furylgermatrane: N→Ge = 2.165 (4) Å) [4].

EXPERIMENTAL

Chemistry

The mixture of ethyl 4-bromobenzoate (22 mmol), $GeBr_4$ (22mmol) and Cu (60 g-at) in 10 ml anhyd. toluene was refluxed 29 h. The reaction mixture was analyzed by GC. The resultant dark yellow solution of 1-(4-ethoxycarbonylphenyl)tribromogermane was transported to a 3-neck flask under Ar. An ethanolic solution (5 ml) of triethylamine (88 mmol) was added dropwise to 1-(4-ethoxycarbonylphenyl)tribromogermane solution in toluene and abs. Et_2O (30 ml), cooled to 0°C, followed by heating to r.t. and refluxing for 1 h. After cooling pentane (10 ml) was added and triethylamine salt was filtered off. Triethanolamine (22 mmol) in an ethanol solution (2 ml) was added dropwise to the filtrate at 0°C. The reaction mixture was stirred at r.t. for 18 h, cooled to 5°C and 1-(4-ethoxycarbonylphenyl)germatrane was filtered off. The single crystals were grown from ethanol by slow evaporation of the solvent, mp.130--131°C. Found (%): C 49.00, H 5.95, N 3.85. $C_{15}H_{21}GeNO_5$. Calculated (%): C 48.96, H 5.75, N 3.81. ^1H NMR (200 MHz, $CDCl_3$) δ ppm: 1.33(3H, s, CH_3), 2.87(6H, t, N-CH_2), 3.84 (6H, t, O-CH_2), 4.31 (2H, q, CH_2) 7.4-8.00 (4H, m, C_6H_4).

Crystallography

Table 1

Crystal data and structure refinement for 1-(4-ethoxycarbonylphenyl)germatrane

Empirical formula	$C_{15}H_{21}GeNO_5$	Index range	-33<=h=<33
Formula weight	367.93		-8<=k<=7
Diffractometer	Nonius KappaCCD		-25<=1<=25
Temperature	293 (2) K	Independent	
Wavelength	0.71073 Å	reflections	7958
Crystal system	monoclinic	Refinement method	Full-matrix least-squares
Space group	P 2_1/c		on F^2
Unit cell	a = 25.9952 (7) Å		
dimensions	b = 6.6862 (1) Å	Data/restraints/parameters	4385/0/401
	c = 19.7546 (5) Å		
	β=111.1743(9)°	Final R-factor [$F^2>3\sigma(F^2)$]	0.077
Volume	3201.72 (13) $Å^3$		
Z	8	R-indices for all data	$wR(F^2)$ = 0.210
Density (calc)	1.527 g/cm^3		R = 0131
Absorption		Largest diff. peak	1.35 e/ $Å^{-3}$
coefficient	1.94 mm^{-1}		
		Weighting scheme	$1/w = \sigma^2 + 0.1F_o^2$
F (000)	1520		
		Programs used	SIR97 [5]
Crystal size	0.05 x 0.32 x		maXus [6]
	0.43mm	Deposition number	
2θ max		CCDC	201583
	55°		

REFERENCES

1. E. Lukevics, L. Ignatovich and S. Belyakov, *J. Organomet. Chem.*, **588**, 222 (1999).
2. E. Lukevics, L. Ignatovich and A. Kemme, *Main Group Metal Chem.*, **25**, 313 (2002).
3. E. Lukevics, L. Ignatovich, T. Shul'ga, O. Mitchenko and S. Belyakov, *J. Organomet. Chem.*, 659, 165 (2002).
4. A. Kemme, L. Ignatovich, E. Lukevics and Ya. Bleidelis, *Latv. PSR Zinatn. Akad. Vestis Khim.* Ser. **1**, 96 (1984).

5. A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni and R. Spagna, *J. Appl. Cryst.*, **32**, 115 (1999).
6. S. Mackay, C.J.Gilmore, C. Edwards, N. Stewart and K. Shankland, *maXus. Computer Program for the Solution and Refinement of Crystal Structures*. Bruker Nonius, The Netherlands, MacScience, Japan & The University of Glasgow, 1999.