NEW SYNTHESIS OF FUNCTIONALLY SUBSTITUTED BIS(SILYLMETHYL)-MERCURY COMPOUNDS

> D. V. Gendin, L. I. Rybin, M. F. Larin, O. A. Vyazankina, and N. S. Vyazankin

UDC 542.91:547.254.9'128

A method is known for obtaining bis(silylmethyl)mercury compounds of type $(R_3SiCH_2)_2Hg$ (R = alkyl, SiR₃) by reacting HgCl₂ with the appropriate Grignard reagents [1-3]. The use of this method is restricted by a very small choice of stable Grignard reagents. For example, due to this, they cannot be used to obtain the above-indicated types of compounds, where R = halogen or alkoxy.

We developed a one-step method for the synthesis of bis(organosilylmethyl)mercury compounds (III) and (IV) in 85-95% yield. The method is based on the photochemical reaction of bis(triethylsilyl)-(I) and bis(triethylgermyl)mercury (II) with chloromethylsilanes $Me_{3}-nX_{n} \cdot SiCH_{2}Cl$.

 $(Et_{3}M)_{2}Hg + 2Me_{3-n}X_{n}SiCH_{2}Cl \xrightarrow{hv} (Me_{3-n}X_{n}SiCH_{2})_{2}Hg$ (I), (II)
(IIIa-d), (IV b-d) M = Si(I), Ge(II) X = Cl (III), OMe(IV); n = 0 (a), 1 (b) 2 (c), 3 (d)

Compounds (III) and (IV) are formed via the chain radical process, which includes the following steps.

chain generation

$$Et_3Ge-Hg-GeEt_3 \xrightarrow{hv} 2Et_3Ge^{\bullet}$$

chain propagation
 $Et_3Ge^{\bullet} + Me_3SiCH_2CI \rightarrow Et_3GeCI + Me_3SiCH_3CI \rightarrow Et_3GECI + Me_3CI \rightarrow Et_3GECI + Me_3GECI + Me_3GECI + Me_3CI \rightarrow Et_3GECI + Me_3CI \rightarrow Et_3GECI + Me_3GECI + Me_3GECI + Me_3GE$

 Me_3SiCH_2 + $(Et_3Ge)_2Hg \rightarrow Me_3SiCH_2HgGeEt_3 + Et_3Ge'.$ Me_3SiCH_2 + $Me_3SiCH_2HgGeEt_3 \rightarrow (Me_3SiCH_2)_2Hg + Et_3Ge'.$

TABLE 1. Physicochemical Properties of Compounds (Me₃-nXnSiCH₂)₂Hg

Com-	Yield, %	bp, C (p, mm Hg)	mp,°C	n ₁)	Found Calculated %					PMR spectrum (C ₆ H ₆ , TMS, δ, ppm)		
pound					с	н	CI	Hg	Si	CH2	CH3	OCH3
(IIIa)	91	51-52	-	1,4860	25,43	6,09	-	53,31	15,11	0,10	0,20	-
		(1)			25,62	5,91		53,49	14,98		ļ	
(IIIb)	95	65 - 66	27-28	1,5127	17,88	3.89	17,06	47,90	13,70	0,18	0,34	-
		(0,02)			17,33	3,88	17,05	48,23	13,51			
(IIIc)	88	82-83	46-48	_	10,63	2,36	_30,86	43,55	12.83	0,30	0,55	
		(0,02)			10,52	2,21	31,05	43,92	12,30			
(IIId)	87	99-101	67-69	_	5.37	0,88	42.84	40,53	11,40	0.41	_	
		(0,02)			4,83	0.81	42,75	40,32	11,29			
(IVb)	84	59-60	-	1,4849	23.40	5.46	_	49.50	14.14	0.08	0.16	3.35
		(0,06)		,	23.61	5.45		49.28	13.80		- ,	
(IVc)	90	81-83	_	1.4746	21.91	5.14	_	45.60	12,95	0.02	0.17	3.44
(- · - /		(0.06)		-, ., 10	21.89	5.05		45.69	12 79	0,02	-,11	-,
(IVa)	79	98-100		_	20.34	4 28		43.33	12.40	0.05		3 52
(-·u/		(0,06)			20.40	4.71		42.58	11.93	v,00		0,04

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2137-2138, September, 1983. Original article submitted December 10, 1982.

chain termination $2Et_3Ge \rightarrow Et_3Ge - GeEt_3$ $2Me_3SiCH_2 \rightarrow (Me_3SiCH_2)_2$ $Et_3Ge + CH_2SiMe_3 \rightarrow Et_3GeCH_2SiMe_3$ (VII)

The radical character of this process is supported by the fact that the products of the recombination of (V) and (VI) and the cross-recombination of (VII), as well as radicals and Hg, were detected as impurities (about 5%). Proof in support of the chain mechanism is the efficient inhibition of the process by a small amount (about 10%) of benzophenone, in whose presence the time for the photodecomposition of (II) increases from 2-3 min to 1.5 h. Previously we had shown [4] that (I) and (II) during photochemical reactions with benzophenones form stable 0-silylated and 0-germylated stable radicals. It is natural to assume that benzophenone functions as a "trap" for silyl and germyl radicals and terminates the chain. The other studied reactions probably proceed by a similar mechanism.

The physicochemical properties of the obtained compounds are given in Table 1. The structure of the products was confirmed by the elemental analysis and the PMR and mass spec-tral data.

EXPERIMENTAL

All of the reactions were run in sealed evacuated ampuls as described in [5]. A DRT-375 quartz Hg lamp was used to irradiate the ampuls. The distance to the light source was 10 cm. Typical experimental procedures are given below.

Bis(trimethylsilylmethyl)mercury (IIIa). To a solution of 2.5 g of Me₃SiCH₂Cl in 10 ml of benzene was added 5.2 g of (II). The mixture was irradiated until the characteristic orange color of (II) disappeared (3 min). Fractional distillation gave 3.4 g (91%) of (IIIa) (see Table 1). The following were also detected in the reaction mixture by GLC: hexaethyl-digermane (V) (~4%), 1,2-bis(trimethylsilyl)ethane (VI) (3%), and (trimethylsilyl)methyltri-ethylgermane (VII) (~3%). We isolated 0.1 g (5%) of Hg. The reaction time is increased to 1.5 h if this reaction is run in the presence of 0.2 g of benzophenone.

Bis(methyldichlorosilylmethyl)mercury (IIIc) was obtained by a similar procedure in 88% yield from 3.7 g of MeCl_SiCH_2Cl and 4.8 g of (I) in 15 ml of hexane.

The other compounds, (III) and (IV), were synthesized in a similar manner.

CONCLUSIONS

A general method was developed for the synthesis of bis(silylmethyl)mercury compounds, which is based on the photoinitiated chain free-radical reaction of bis(triethylsilyl)- and bis(triethylgermyl)mercury with chloromethylsilanes.

LITERATURE CITED

- 1. D. Seyferth and W. Freyer, J. Org. Chem., 26, 2604 (1961).
- F. Glockling, S. R. Stobart, and J. J. Sweeney, J. Chem. Soc. Dalton Trans., <u>19</u>, 2029 (1973).
- 3. M. Kumada and M. Ishikawa, J. Organomet. Chem., 6, 451 (1966).
- D. V. Gendin, T. I. Vakul'skaya, O. A. Kruglaya, and G. G. Furin, Izv. Akad. Nauk SSSR, Ser. Khim., 2323 (1979).
- 5. N. S. Vyazankin, G. A. Razuvaev, O. A. Kruglaya, and G. S. Semchikova, J. Organomet. Chem., <u>6</u>, 474 (1966).