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PHOTOCHEMICAL ADDITION OF TRIALKYLSILANETHIOLS AND TRIALKYLGERMANETHIOLS TO ACETYLENIC COMPOUNDS

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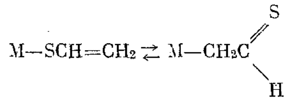
Previously we had described methods for the preparation of organyl(alken-1-ylthio)silanes, organyl(alken-1-ylthio)germanes, and organyl(alken-1-ylthio)stannanes $R_{4-n}M(SCHR'=CHR'')_n$ (where M = Si, Ge, Sn; R = alkyl; R' = H, alkyl; R'' = H, alkyl, aryl) [1]. It was shown that compounds of this type, in contrast to their oxygen analogs, are stable and under ordinary conditions are incapable of tautomeric transformations according to the scheme:



$$M{-}SCH{=}CH_2 \rightleftarrows M{-}CH_2C\begin{matrix}{\nearrow S}\\ {\searrow H}\end{matrix}$$

New methods were developed for the synthesis of the alkenylthio derivatives of the Group IVB elements, and we were the first to effect the photochemical addition of triethylsilanethiol and triethylgermanethiol to monosubstituted acetylenes, including to trialkylethynylsilanes and trialkylethynylgermanes. The reaction proceeds easily by the general scheme:

$$RC{\equiv}CH + HSM(C_2H_5)_3 \xrightarrow{h\nu} RCH{=}CHSM(C_2H_5)_3 \quad \text{(I)—(VIII)}$$
$$M = Si\ \text{(I), (II), (III)},\ Ge\ \text{(IV), (VIII)};$$
$$R = (CH_3)_3C\ \text{(I), (V)},\ C_6H_5\ \text{(II), (VI)},\ Si(CH_3)_3\ \text{(III)},$$
$$Si(C_2H_5)_3\ \text{(VII)},\ (C_2H_5)_3Ge\ \text{(IV), (VIII)}$$

The yield of the products is usually close to quantitative. The properties of the obtained compounds (I)-(VIII) are given in Table 1. These compounds are either colorless or yellowish mobile liquids with a specific odor. Based on the NMR spectral data (Table 2), they are a mixture of the cis and trans isomers, with a predominance of the latter. It was also established by this method that in the temperature range 20-200° they do not undergo the metallotropic rearrangements that are characteristic for their oxygen analogs [2]. The frequencies of the stretching vibrations of the double bond in compounds (I)-(VIII) are given in Table 1.

EXPERIMENTAL METHOD

The NMR spectra were obtained on a Tesla BS-487C spectrometer for 10-20% CCl_4 solutions at 20°, using HMDS as the internal standard. The accuracy of measuring the chemical shifts was ~0.01 ppm. The IR spectra were taken on a UR-10 spectrophotometer as a thin layer.

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TABLE 1. Properties of Synthesized Compounds

Compound	Yield, %	Yield, %	Bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	Found, %					Empirical formula	Calculated, %					IR spectrum ($\nu_{C=C}$, cm^{-1})
						C	H	S	Si	Ge		C	H	S	Si	Ge	
(I)	$(C_2H_5)_3SiSCH{=}CHC(CH_3)_3$	96	94—96 (6)	1,4795	0,8660	62,64	11,56	13,92	12,39	—	$C_{12}H_{26}SSi$	62,53	11,37	13,91	12,14	—	1605
(II)	$(C_2H_5)_3SiSCH{=}CHC_3H_5$	85	147—148 (5)	1,5680	0,9822	67,42	8,74	12,70	11,07	—	$C_{14}H_{22}SSi$	67,18	8,87	12,74	11,12	—	1600
(III)	$(CH_3)_3SiCH{=}CHSSi(C_2H_5)_3$	99	94 (3)	1,4864	0,8733	53,41	10,68	13,01	22,83	—	$C_{11}H_{26}SSi_2$	53,58	10,63	13,00	22,78	—	1550
(IV)	$(C_2H_5)_3GeCH{=}CHSSi(C_2H_5)_3$	93	144—147 (2)	1,5038	1,0165	50,82	9,81	9,41	8,37	21,84	$C_{14}H_{32}SSiGe$	50,47	9,69	9,62	8,43	21,80	1530, 1565
(V)	$(C_2H_5)_3GeSCH{=}CHC(CH_3)_3$	72	88—90 (4)	1,4958	1,0278	52,56	9,50	11,36	—	26,42	$C_{12}H_{26}GeS$	52,41	9,53	11,65	—	26,44	1605
(VI)	$(C_2H_5)_3GeSCH{=}CHC_6H_5$	90	138—140 (2)	1,5905	1,1459	58,00	7,70	11,22	—	24,20	$C_{14}H_{22}SGe$	57,12	7,53	10,87	—	24,16	1595
(VII)	$(C_2H_5)_3GeSCH{=}CHSi(C_2H_5)_3$	55	147—148 (2)	1,5068	1,0259	50,40	9,93	9,34	8,29	21,40	$C_{11}H_{32}SSiGe$	50,47	9,69	9,62	8,43	21,80	1535, 1582
(VIII)	$(C_2H_5)_3GeSCH{=}CHGe(C_2H_5)_3$	78	137—140 (1)	1,5175	1,1498	44,87	8,67	8,43	—	38,34	$C_{14}H_{32}SGe_2$	44,52	8,48	8,54	—	38,44	1537, 1572

TABLE 2. Parameters of NMR Spectra of Compounds $RCH_\alpha = CH_\beta SM(C_2H_5)_3$

R	M	Chemical shift τ, ppm*							$^3J_{H_\alpha H_\beta}$, Hz		Ratio of isomers, trans/cis
		trans Isomer		cis Isomer		R	M (C_2H_3)				
		H_α	H_β	H_α	H_β		CH_2	CH_3	trans	cis	
$C(CH_3)_3$	Si	4,11	4,34	—	—	9,00	9,28	9,03	14,9	—	—
C_6H_5	Si	3,49	3,29	3,88	3,50	2,44–3,28	9,21	9,01	15,0	10,6	2/1
$Si(CH_3)_3$	Si	3,89	3,53	4,22	3,14	9,95 (trans) 9,79 (cis)	9,22	8,99	17,6	12,2	6/1
$Ge(C_2H_5)_3$	Si	3,83	3,74	4,16	3,15	9,24 (CH_2) 9,00 (CH_3)	9,24	9,00	17,5	11,2	7/1
$C(CH_3)_3$	Ge	4,15	4,28	—	—	9,00	9.03	8,90	15,1	—	—
C_6H_5	Ge	3,44	3,31	3,84	3,55	2,32–3,09	8,95	8,90	16,5	11,0	2/1
$Si(C_2H_5)_3$	Ge	4,06	3,56	4,45	3,05	9,48 (CH_2) 9,06 (CH_3)	8,96	8,91	18,0	12,0	8/1
$Ge(C_2H_5)_3$	Ge	3,92	3,69	4,23	3,11	9,23 (CH_2) 8,99 (CH_3)	8,97	8,90	17,5	11,0	8/1

*The resonance of the olefinic protons is depicted by a multiplet of the AB type.

Triethyl-(β-triethylsilylthio)germane. A mixture of 1.1 g (5.9 mmoles) of triethylethynylgermane and 0.7 g (4.7 mmoles) of triethylsilanethiol in a sealed Pyrex glass ampul was irradiated with the UV light from a PRK-2 lamp at 50°. Vacuum-distillation gave 1.45 g (93%) of adduct (IV), bp 144-147° (2 mm): n_D^{20} 1.5038; d_D^{20} 1.0165.

Compounds (I)-(VIII) were synthesized in a similar manner.

CONCLUSIONS

The addition reaction of trialkylsilane- and trialkylgermanethiols leads to the formation of the corresponding trialkylsilyl and trialkylgermyl (β-organyl)vinyl sulfides in high yield.

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REACTION OF DIALKYLPHOSPHOROUS ACIDS WITH 2,2-DIMETHYL-1,3-INDANDIONE

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Previously the phosphorus-containing derivatives of 1,3-indandione could not be obtained by the reaction of the mono- and dihalo derivatives of 1,3-indandione with sodium diethyl phosphite or triethyl phosphite [1]. Attempts to insert the phosphono group in the 2 position of 1,3-indandione ended in failure. Subsequently it proved that the dialkylphosphorous acids react well with 1,3-indandione derivatives at the carbonyl group. The results of studying the reaction of 2,2-dimethyl-1,3-indandione (I) with diethylphosphorous (II) and di-n-butylphosphorous (IIa) acids are reported in the present communication.

2,2-Dimethyl-3-hydroxyindan-1-one-3-diethylphosphonate (III) and 2,2-dimethyl-3-hydroxyindan-1-one-3-di-n-butylphosphonate (IIIa) were isolated when the reaction was run at room temperature in the presence of triethylamine. Infrared spectrum of (III) (ν, cm^{-1}): 710, 750, 788, 948 (m;) 982 (s); 1025, 1058, 1077 (v.s.); 1165 (m) (POC_2H_5); 1222 (v.s) (P =O); 1610 (m); 1725 (v.s) (C=O); 3283 (v.s) (OH); δ_{31P} −25 ppm (relative to 85% H_3PO_4). Based on the IR spectrum (III) has the hydrogen bond $>P=O\ldots HO$.

A. M. Butlerov Chemical Institute of the V. I. Ul'yanov-Lenin Kazan State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1416-1418, June, 1976. Original article submitted December 2, 1975.

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