REACTION OF ARYLARSONIC ACIDS WITH ORGANYLALKOXY- AND ORGANYLACETOXY-SILANES

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Phenylarsonium acid reacts with triphenylchlorosilane [1, 2] or trialkyl- and triarylsilanols [3] to form bis(triorganylsilyl)phenylarsonates (I). We have developed a convenient method for the preparation of (I) with yields up to 60% by the reaction of phenylarsonic acid with triorganylalkoxy- or triorganylacetoxysilanes at 60-120°C according to the following scheme:

$$\begin{array}{l} C_{6}H_{5}AsO(OH)_{2} + 2ROSiR^{1}R_{2}^{2} \rightarrow C_{6}H_{5}AsO(OSiR^{1}R_{2}^{2})_{2} + 2ROH \\ (Ia, b) \\ R = R^{1} = CH_{3}, \ R^{2} = n - C_{3}H_{7} \ (a); \ R = CH_{3}C(O), \ R^{1} = R^{2} = C_{2}H_{5} \ (b). \end{array}$$

The structures of (Ia) and (Ib) were supported by PMR and IR spectroscopy and mass spectrometry.

In contrast to (Ia) and (Ib), bis(trimethylsilyl)- and bis(dimethylsilyl)phenylarsonates are unstable compounds, which decompose upon distillation *in vacuo* to give a quantitative yield of phenylarsonic acid anhydride and hexamethyldisiloxane or tetramethyldisiloxane, respectively. We were unable to isolate bis(trimethylsilyl)phenylarsonate by the reaction of phenylarsonic acid with hexamethyldisilazane, which indicates the instability of bis(trimethylsilyl)- and bis(dimethylsilyl)phenylarsonates.

The reaction of phenylarsonic acid with organyldialkoxy-, organyltrialkoxy-, or tetraalkoxysilanes leads to dialkylphenylarsonates (II)

$$\begin{array}{l} C_{6}H_{5}AsO(OH)_{2} + (RO)_{n}SiR_{4-n}^{1} \rightarrow C_{6}H_{5}AsO(OR)_{2} + [R^{1}(RO)SiO]_{m} \\ (II) \\ + R^{1}(RO)_{2}Si[OSi(OR)R^{1}]_{m}OSi(RO)_{2}R^{1} + 2ROH \\ R = CH_{3}, C_{2}H_{5}; R^{1} = CH_{3}, CH_{2} = CH; n = 2-4; m = 0, 1, 4. \end{array}$$

This reaction [4] permits the preparation of phenylarsonate esters in preparative yield. The compositions and structures of the linear and cyclic organylsiloxanes, (III) and (IV), formed in this reaction, were confirmed by chromato-mass spectrometry.

EXPERIMENTAL

The mass spectra were taken on a Varian MAT-212 mass spectrometer at 70 eV. Gas-liquid chromatography was carried out on a Varian 3700 chromatograph using a column packed with SE-54 and helium as the gas carrier. The IR sepctra were taken neat on a Specord 75-IR spectrometer at 400-4000 cm⁻¹. The PMR spectra were taken on a Tesla BS-497 spectrometer at 100 MHz. The compounds were studied as 10% solutions in CDCl₃.

<u>Bis(methyldipropylsilyl)phenylarsonate (Ia).</u> A mixture of 16.0 g (0.1 mole) methyldipropylmethoxysilane and 10.1 g (0.05 mole) phenylarsonic acid was slowly distilled on an oil bath until methanol was no longer collected. The residue was distilled *in vacuo* to give 13.7 g (60%) (Ia), bp 195°C (2 mm), n_D^{20} 1.4853, d_4^{20} 1.0727. Found: Si, 12.08; As, 16.33%. Calculated for $C_{20}H_{39}O_3AsSi_2$: Si, 12.25; As, 16.33%.

<u>Bis(triethylsilyl)phenylarsonate (Ib).</u> A mixture of 15.7 g (0.9 mole) triethylacetoxysilane and 8.1 g (0.04 mole) phenylarsonic acid was heated until acetic acid was no longer distilled off. Vacuum distillation of the residue gave 9.4 g (54.7%) (Ib), bp 173-175°C

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(2 mm), n_{D}^{20} 1.4942, d_{4}^{20} 1.0151. Found: Si, 13.00; As, 17.34%. $C_{18}H_{35}O_{3}AsSi_{2}$. Calculated: Si 13.05; As, 17.40%.

The reaction with trimethyl- and dimethylacetoxysilanes is carried out by analogy.

<u>Dimethylphenylarsonate.</u> A mixture of 15.3 g (0.1 mole) Si(OMe), and 10.1 g (0.05 mole) phenylarsonic acid was heated until the acid was fully dissolved and 4.0 ml (100%) MeOH was separated. Vacuum distillation of the residue gave 7.6 g (66%) $C_6H_5As(OCH_3)_2$, bp 105°C (0.2 mm), n_D^{20} 1.5396, d_4^{20} 1.4212 [5]. IR spectrum (ν , cm⁻¹): 650 (AsO₂), 957 (As=O), 1008 (O-C), 1022 (O-C), 1120 [CH₃], 1449 (C₆H₅), 2838 [CH₃], 2900 (C-H), 2945 [CH₃], 2975 (C-H). PMR spectrum (δ , ppm): 3.82 (OCH₃), 7.50-7.80 (C₆H₅As).

The yields of dimethylphenylarsonate in the reaction of phenylarsonic acid with dimethyldimethoxysilane and vinyltrimethoxysilane were 61 and 63%, respectively. Analogously, by the reaction of phenylarsonic acid with vinyl(triethoxy)silane or $Si(OC_2H_5)_4$, we obtained diethylphenylarsonate with yields, respectively, of 52 and 65%, bp 125-127°C (1 mm), $n_D^{2^0}$ 1.5150 [6]. PMR spectrum (δ , ppm): 4.19 m (CH₂), 1.32 t (CH₃), 7.56-7.84 (C₅H₅AS). Mass spectrum (m/z): 258(3) M⁺, 213(54) (M-C_2H_50)+, 169(100) [C₆H₅AS(0)(OH)]+.

The mass spectra (m/z) of the other products of the reaction of vinyltrimethoxy- and vinyltriethoxysilane with phenylarsonic acid. $[C_2H_3(CH_3O)_2Si]_2O: 250(1)(M^+°), 223(93)(M - C_2H_3)^+, 219(31)(M - CH_3O)^+, 218(100)(M - CH_3OH)^+, 193(17)(M - CH_3O - C_2H_2)^+ C_2H_3(CH_3O)Si[OSi(CH_3O)_2^- C_2H_3]_2: 352(2)(M^+°), 325(100)(M - C_2H_3)^+, 321(21)(M - CH_3O)^+, 320(47)(M - CH_3OH)^+, 295(20)(M - CH_3O - C_2H_2)^+. [C_2H_3(MeO)Si]_4: 408(4)(M^+°), 381(100)(M - C_2H_3)^+, 377(19)(M - CH_3O)^+, 376(32)(M - CH_3OH)^+, 351(30)(M - CH_3O - C_2H_2)^+. [C_2H_3(C_2H_5O)_2Si]_2O: 306(2)(M^+°), 279(40)(M - C_2H_3)^+, 261(100)(M - C_2H_5O)^+, 260(80)(M - C_2H_5OH)^+, 235(35)(M - C_2H_5O - C_2H_2)^+. [C_2H_3(C_2H_5O)Si[OSi(C_2H_5O)_2C_2H_3]_2: 422(3)(M^+°), 395(31)(M - C_2H_3)^+, 377(100)(M - C_2H_5O)^+, 376(59)(M - C_2H_5OH)^+.$

CONCLUSIONS

The reaction of phenylarsonic acid with trialkylalkoxy- or trialkylacetoxysilanes leads to the formation of bis(trialkylsilyl)phenylarsonates. Bis(trimethylsilyl)- and bis(di-methylsilyl)phenylarsonates are thermally unstable and decompose upon separation.

2. The reaction of phenylarsonic acid with organylalkoxy- or tetraalkoxysilanes is a convenient method for the preparation of dialkylphenylarsonates.

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