Organometallic Chemistry

Homolytic addition of polyhaloalkanes to α-vinyloxy-ω-trialkylstannoxyalkanes as a new route to 2-perhaloalkylmethyl-substituted 1,3-dioxacyclanes

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Photoinduced reactions of α-vinyloxy-ω-trialkylstannoxyalkanes, CH_2=$CHO(CH_2)_nOSnEt_3$ (n = 2 to 4), with polyhaloalkanes result in 2-perhaloalkylmethyl-substituted 1,3-dioxacyclanes.

Key words: α-vinyloxy-ω-trialkylstannoxyalkanes, polyhaloalkanes, photoinduced reactions; 1,3-dioxacyclanes.

The photochemical reaction of polyhaloalkanes R_YI (R_Y = CCl_3, CF_3, C_3F_7) with trialkylalkenyloxystannanes CH_2=$CH(CH_2)_nOSnR_3$ (R = Et, Bu; n = 1, 3) gives the corresponding polyhaloalkyl-substituted oxiranes and tetrahydrofurans.[1] The mechanism of this reaction involves homolytic addition of a polyhaloalkane to the double bond followed by intramolecular nucleophilic substitution of a halogen atom. One of the main factors determining the yield of the products is the reactivity of the C—Hal bond, which is formed in the first step, in the nucleophilic processes. The C—Hal bond displays a particularly high reactivity in α-haloesters, *i.e.*, in the Hal—C—O— moiety.

We studied a photochemical reaction of α-vinyloxy-ω-trialkylstannoxyalkanes with polyhaloalkanes and methyl monobromoacetate. One could expect that this reaction would give the corresponding highly reactive adducts capable of cyclization through elimination of a trialkylhalostannane.

The starting compounds **1**—**3** (Tables 1 and 2) were obtained by the reaction of trialkylmethoxystannanes with monovinyl ethers of diols.

$$HC{\equiv}CH + HO(CH_2)_nOH \longrightarrow$$

$$\longrightarrow CH_2{=}CHO(CH_2)_nOH \xrightarrow[-MeOH]{MeOSnEt_3}$$

$$\longrightarrow CH_2{=}CHO(CH_2)_nOSnEt_3$$

1—3

n = 2 (**1**), 3 (**2**), 4 (**3**)

The photochemical reactions of α-vinyloxy-ω-trialkylstannoxyalkanes **1**—**3** with polyhaloalkanes were carried out by UV irradiation of an equimolar mixture of the reagents in sealed glass tubes. The reactions were accompanied by intense self-heating and ceased in sev-

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Table 1. Physicochemical constants of *O*-(trialkylstannyl)monovinyl ethers of diols **1—3**

Compound	Yield (%)	B.p./°C (*p*/Torr)	n_D^{20}
$Et_3SnO(CH_2)_2OCH=CH_2$ (**1**)	96	89—92 (1)	1.4837
$Et_3SnO(CH_2)_3OCH=CH_2$ (**2**)	95	98—99 (3)	1.4781
$Et_3SnO(CH_2)_4OCH=CH_2$ (**3**)	82	122—124 (4)	1.4756

Table 2. Parameters of the ^1H NMR spectra of *O*-(trialkylstannyl)monovinyl ethers of diols **1—3**

Compound	^1H NMR, δ
1	1.14 (m, 15 H, $(C_2H_5)_3Sn$); 3.70—4.14 (m, 6 H, $-CH_2CH_2-$ and $=CH_2$); 6.45 (m, 1 H, $-OCH=$)
2	1.15 (m, 15 H, $(C_2H_5)_3Sn$); 1.69 (m, 2 H, $-CH_2-$); 3.71 (m, 4 H, $-OC\underline{H}_2CH_2C\underline{H}_2O-$); 6.46 (m, 1 H, $-OCH=$); 3.94—4.18 (m, 2 H, $=CH_2$)
3	1.15 (m, 15 H, $(C_2H_5)_3Sn$); 1.65 (m, 4 H, $-CH_2CH_2-$); 3.68 (m, 4 H, $-OC\underline{H}_2CH_2CH_2C\underline{H}_2O-$); 6.42 (m, 1 H, $-OCH=$); 3.92—4.14 (m, 2 H, $=CH_2$)

eral minutes. The derivatives of 1,2-ethanediol (n = 2), 1,3-propanediol (n = 3), and 1,4-butanediol (n = 4) gave the corresponding 2-perhaloalkylmethyl-1,3-dioxacycloalkanes **4—9** (Tables 3 and 4).

$$R_YX + CH_2{=}CHO(CH_2)_nOSnEt_3 \xrightarrow{h\nu}$$

$$\longrightarrow Et_3SnX + R_YCH_2{-}\underset{\displaystyle O(CH_2)_nO}{\underbrace{CH}}$$

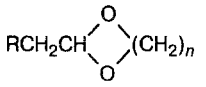
4—9

4: X = Br, R_Y = CCl_3, n = 2
5: X = Br, R_Y = CCl_3, n = 4
6: X = Br, R_Y = $MeOOCCH_2$, n = 2
7: X = I, R_Y = C_3F_7, n = 2
8: X = I, R_Y = C_3F_7, n = 3
9: X = I, R_Y = C_3F_7, n = 4

A similar reaction of stannylated monovinyl ethers of 1,6-hexanediol and diethylene glycol with polyhaloalkanes gave oily undistillable and uncrystallizable products, which we did not study.

It was more difficult to reveal the mechanism for the formation of 1,3-dioxacycloalkanes **4—9** than in the case of the reactions of alkenyloxystannanes with polyhaloalkanes. For example, the difference between the yields of cyclic products in the case of bromotrichloromethane and heptafluoroiodopropane is not sufficiently high to make a conclusion on the effect of the nucleophilicity of the leaving group on the intramolecular nucleophilic

Table 3. Physicochemical characteristics of 1,3-dioxacycloalkanes **4—9**



Compound	R	n	Yield (%)	B.p./°C (*p*/Torr)	n_D^{20}
4	CCl_3	2	64.0	72—73 (3)	1.4844
5	CCl_3	4	76.0	82—84 (1.5)	1.4904
6	$MeOOCCH_2$	2	67.5	88—91 (10)	1.4501
7	C_3F_7	2	97.0	63—65 (40)	1.3442
8	C_3F_7	3	83.0	65—68 (2)	1.3537
9	C_3F_7	4	78.0	61—62 (1)	1.3620

Table 4. Parameters of ^1H NMR spectra and mass spectra of 1,3-dioxacycloalkanes **4—9**

Compound	^1H NMR, δ	MS, *m/z*
4	3.07 (d, 2 H, CCl_3CH_2); 5.26 (t, 1 H, $-CH_2C\underline{H}$); 3.95 (m, 4 H, $-OCH_2CH_2O-$)	208, 206, 204, 73
5	2.99 (d, 2 H, CCl_3CH_2); 5.11 (t, 1 H, $-CH_2C\underline{H}$); 3.77 (m, 4 H, $-OC\underline{H}_2CH_2CH_2C\underline{H}_2O-$); 1.73 (m, 4 H, $-CH_2C\underline{H}_2C\underline{H}_2CH_2-$)	232, 101
6	3.66 (s, 3 H, CH_3); 2.41 (t, 2 H, $-OOCCH_2-$); 2.00 (m, 2 H, $-CH_2C\underline{H}_2CH-$); 4.92 (t, 1 H, $-CH_2C\underline{H}$); 3.69 (m, 4 H, $-OCH_2CH_2O-$)	160, 129, 73
7	2.47 (t, 2 H, $C_3F_7CH_2$); 5.24 (t, 1 H, $-CH_2C\underline{H}$); 3.96 (m, 4 H, $-OCH_2CH_2O-$)	256, 211, 72
8	2.39 (t, 2 H, $C_3F_7CH_2$); 4.94 (t, 1 H, $-CH_2C\underline{H}$); 4.13—3.79 (m, 4 H, $-OC\underline{H}_2CH_2CH_2C\underline{H}_2O-$); 1.36 (m, 2 H, $-CH_2C\underline{H}_2CH_2-$)	
9	2.36 (t, 2 H, $C_3F_7CH_2$); 5.12 (t, 1 H, $-CH_2C\underline{H}$); 3.77 (m, 4 H, $-OC\underline{H}_2CH_2CH_2C\underline{H}_2O-$); 1.72 (m, 4 H, $-CH_2C\underline{H}_2C\underline{H}_2CH_2-$)	284, 212, 101

substitution. We failed to record the ^1H NMR spectrum of the intermediate addition product even when the reaction mixture was irradiated directly in the probe of the NMR spectrometer at −40 °C. This can be explained both by the high reactivity of the resulting addition product, which is an α-haloester, and by intramolecular cyclization of the intermediate, the radical aduct $R_YCH_2C^{\cdot}HO(CH_2)_nOSnR_3$. The latter assumption is quite reasonable, since in this case the rate of transfer of the Hal atom should be lower than that in a similar reaction with trialkylalkenyloxystannanes due to stabilization of the radical center by the O atom located in the α-position.

Experimental

GLC analyses were carried out on a Tsvet-126 chromatograph (a thermal conductivity detector; helium as the carrier gas; 3000×4 mm glass columns; Chromaton-N-AW-HMDS sorbent, 0.2—0.25 mm grain size, impregnated with 10 % PMS-1000).

^{1}H NMR spectra were obtained on a Tesla BS-567 A spectrometer (100 MHz). The chemical shifts were measured to within 0.01 ppm. Mass spectra were recorded on a Varian MAT-212 spectrometer at an ionizing energy of 70 eV.

***O*-(Trialkylstannyl)monovinyl ethers of diols** were obtained by transesterification of trialkylmethoxystannanes with the corresponding monovinyl ethers of diols by the known procedure. The physicochemical constants of the compounds synthesized are reported in Table 1, and the parameters of the ^{1}H NMR spectra are presented in Table 2.

Reaction of *O*-(trialkylstannyl)monovinyl ethers of diols with polyhaloalkanes and methyl monobromoacetate. An equimolar mixture of *O*-(trialkylstannyl)monovinyl ether of diol and polyhaloalkane was placed in a glass tube. The tube was purged with argon and irradiated with UV light (DRT-400 lamp) for 6 h at 30 °C. The target product was isolated by distillation *in vacuo*. The yields and the main physicochemical parameters of the resulting 1,3-dioxacycloalkanes are given in Table 3, and their spectroscopic parameters are presented in Table 4.

References

1. P. V. Arbuzov, V. I. Rakhlin, R. G. Mirskov, B. Z. Shterenberg, and M. G. Voronkov, *Metalloorg. Khim.*, 1989, **2**, 889 [*Organomet. Chem. USSR*, 1989, **2**, 465 (Engl. Transl.)].

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