BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 777—780 (1971)

γ-Induced Addition of Trialkyltin Hydrides to Unsaturated Esters

Jitsuo Tsurugi, Masaru Iida,* Ren Nakao, Tsugio Fukumoto, and Niro Murata*
Department of Chemistry, Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka
* *Department of Applied Chemistry, University of Osaka Prefecture, Mozuume-machi, Sakai, Osaka*

(Received July 18, 1970)

γ-Induced hydrostannation of ethyl acrylate, allyl acetate, and vinyl acetate with triethyltin and tri-*n*-butyltin hydrides was attempted. The hydrostannation of ethyl acrylate and allyl acetate gave the corresponding adducts in almost quantitative yield. (2-Acetoxyethyl)-tri-*n*-butyltin expected from hydrostannation of vinyl acetate with tri-*n*-butyltin hydride could not be isolated. However, NMR and IR spectra indicated the formation of the adduct, which was found to decompose into ethylene and tri-*n*-butyltin acetate. The decomposition of the adduct was discussed in comparison with other adducts.

The addition reaction of organotin hydrides to unsaturated bonds is known as hydrostannation and extensively studied.[1,2] However, hydrostannation with γ-irradiation has not been reported so far. In this paper we report the γ-induced hydrostannation of ethyl acrylate, allyl acetate, and vinyl acetate with triethyltin and tri-*n*-butyltin hydrides. The hydrostannation of vinyl acetate and tri-*n*-butyltin hydride was found not to give the expected adduct, (2-acetoxyethyl)-tri-*n*-butyltin, but to yield tri-*n*-butyltin acetate. No successful synthesis of the expected adduct is found in literature. The reason why this adduct cannot be isolated is given.

Results and Discussion

γ-Induced Hydrostannation. A mixture of 1 : 2 molar ratio of tri-*n*-butyltin hydride and vinyl acetate gave a curdy product after being subjected to irradiation. The amount of the product seems proportional

---

[1] Y. Nagai, *Kagaku no Ryoiki*, **23**, 233 (1969).

[2] H. G. Kuivila, "Advances in Organometallic Chemistry," Vol. 1, ed. by F. G. A. Stone and R. West, Academic Press, New York, N. Y. (1964), p. 47.

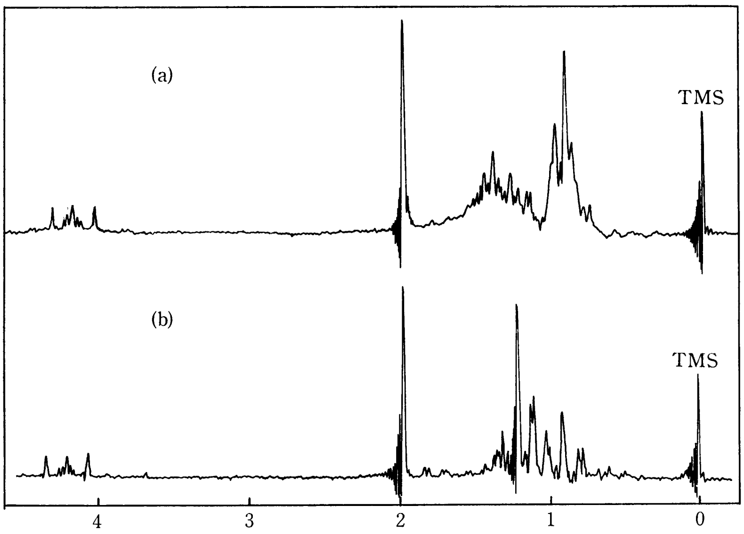


Fig. 1. The NMR spectra in CCl_4 of irradiated mixture of run 4 (a) and of (2-acetoxyethyl)-triethyltin (b).

to irradiation dose in the range 10^5—10^7R. This product was identified as polyvinyl acetate by IR spectrum. An equimolar mixture of trialkyltin hydride and the unsaturated ester was used in the experiments, because the mixture gave no curdy product under irradiation of similar doses. Yields of the 1 : 1 adducts are summarized in Table 1. Table 1 indicates that the hydrostannation proceeds almost quantitatively in runs 1 and 2. From the result we can write the reaction as free radical 1 : 1-β-addition, the detailed mechanims of which has been reviewed.[2] We assume that the equation

$$R_3SnH + CH_2{=}CHR' \rightsquigarrow R_3SnCH_2CH_2R' \tag{1}$$

would still be applicable to runs 3 and 4, and that adduct **4** would decompose completely and **3** partially during separation procedures.

In order to verify this we examined the irradiated mixture of run 4 by NMR and IR methods. Fig. 1a shows the NMR spectrum of irradiated mixture in carbon tetrachloride solution at 60 MHz. In comparison with NMR signals of adduct **3** (Fig. 1b), the superimposed triplet centered at about 0.9 ppm can be assigned to the methylenes bonded to the tin atom, and the remaining multiplet in the high field to butyl methylenes and methyls. The singlet signal at 2.0 ppm is assigned to acetyl protons. In the lower field, complicated signals appear at about 4.2 ppm. From the signal shift and integrated intensity, this is assigned to the methylene protons bonded to the acetyl group. The NMR spectrum of adduct **3** shows similar signals except for the alkyl substituents. Figure 2 shows the IR spectrum of irradiated mixture of run 4. The key bands indicating the existence of the saturated acetylate observed as two strong bands were attributable to the C=O stretching vibration in 1735 cm^{-1} and C–O–C antisymmetrical vibration in 1237 cm^{-1}. The spectrum is devoid of absorption bands due to the carbonyls of tri-*n*-butyltin acetate (1642 cm^{-1}) and vinyl acetate (1760 cm^{-1}). From IR and NMR spectral evidences, hydrostannation is considered to occur also in the case of run 4.

TABLE 1. γ-INDUCED HYDROSTANNATION OF UNSATURATED ESTERS $CH_2{=}CHR'$ WITH TRIALKYLTIN HYDRIDES R_3SnH IN 1:1 MOLAR RATIO

Run No.	R in R_3SnH	R′ in $CH_2{=}CHR'$	Dose rate (R/hr $\times 10^5$)	Dose ($R\times 10^7$)	1:1 Adduct No.[a)]	Yield[b)]
1	n-C_4H_9	$-COOC_2H_5$	3.0	1.2	1	96
2	n-C_4H_9	$-CH_2OCOCH_3$	3.0	1.2	2	98
3	C_2H_5	$-OCOCH_3$	2.5	1.0	3	60
4	n-C_4H_9	$-OCOCH_3$	3.0	1.2	4	0

a) adduct 1: (2-carboethoxyethyl)-tri-*n*-butyltin $(n\text{-}C_4H_9)_3SnCH_2CH_2COOC_2H_5$
adduct 2: (3-acetoxypropyl)-tri-*n*-butyltin $(n\text{-}C_4H_9)_3SnCH_2CH_2CH_2OCOCH_3$
adduct 3: (2-acetoxyethyl)-triethyltin $(C_2H_5)_3SnCH_2CH_2OCOCH_3$
adduct 4: (2-acetoxyethyl)-tri-*n*-butyltin $(n\text{-}C_4H_9)_3SnCH_2CH_2OCOCH_3$

b) Gas chromatographic determination for adducts **1** and **2**, and distillation for **3** and **4**. The application of the former to **3** resulted in complete decomposition.

Decomposition of the Adduct 4. Distillation of the irradiated mixture of run 4 gave white needles, bp

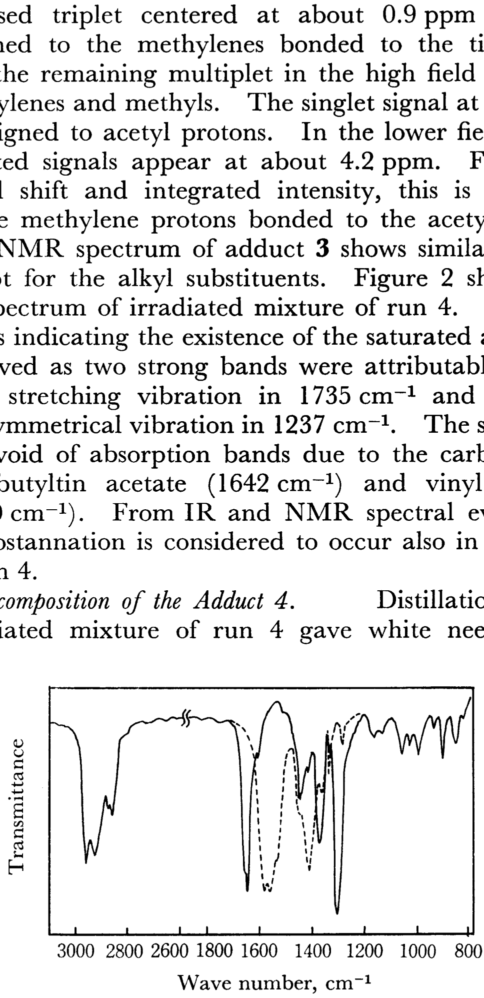


Fig. 2. The IR spectra in CCl_4.
—— irradiated mixture of run 4
······ non-irradiated mixture of tri-*n*-butyltin hydride and vinyl acetate

90—100°C/0.001 mmHg, mp 84.8°C (lit,[3] 84.5—85°C), identified as tri-*n*-butyltin acetate by IR and NMR and elemental analysis. Qualitative glpc analysis (at 180°C column temperature) of the irradiated mixture indicates the presence of tri-*n*-butyltin acetate but no other compounds. These results suggest the following equation for the decomposition of adduct **4**.

$$(n\text{-}C_4H_9)_3SnCH_2CH_2OCOCH_3 \longrightarrow (n\text{-}C_4H_9)_3SnOCOCH_3 + CH_2{=}CH_2 \qquad (2)$$

Evolution of ethylene was qualitatively observed by gas analysis from the irradiated mixture kept standing for several weeks at room temperature. Addition of acetic acid or anhydride was found effective for the decomposition of adduct **4**. After being kept standing for 24 hr at room temperature in an open vessel, tri-*n*-butyltin acetate was filtered and weighed. The result is shown in Fig. 3.

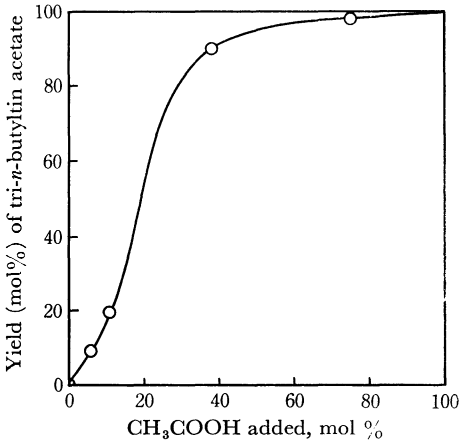
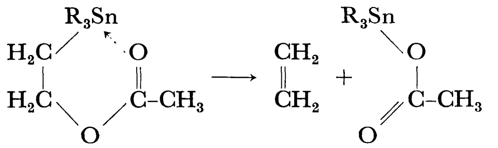


Fig. 3. Effect of the addition of acetic acid to adduct **4**.
One mole of adduct **4** was assumed to be produced from irradiated mixture of each one mole of starting materials.

The results in Table 1 indicate that only the adducts resulting from trialkyltin hydride and vinyl acetate decompose during distillation[4] or gas chromatography as compared with almost quantitative yields of the adducts **1** and **2**. Hence, the decomposition can be ascribed to intramolecular formation of cyclic transition state followed by elimination of ethylene and simultaneous formation of Sn–O bond. In a closed vessel



(3)

the presence of ethylene evolved suppresses the decomposition. Distillation, gas chromatography, heating or being left at room temperature in an open vessel allows ethylene to evolve out of the system, and shifts the equilibrium to the right side.

Van der Kerk *et al.*[5] reported that triphenyltin hydride with vinyl acetate yielded the adduct quantitatively. The structure of R in $R_3SnCH_2CH_2OCOCH_3$ seems to play an important role. In the cleavage reaction of tetraalkyltin with chloroacetic acid,

$$(n\text{-}C_3H_7)_4Sn + ClCH_2COOH \longrightarrow (n\text{-}C_3H_7)_3SnOCOCH_2Cl + n\text{-}C_3H_8 \qquad (4)$$

$$(i\text{-}C_3H_7)_4Sn + 2ClCH_2COOH \longrightarrow (i\text{-}C_3H_7)_2Sn(OCOCH_2Cl)_2 + 2i\text{-}C_3H_8 \qquad (5)$$

Sasin *et al.*[6] interpreted Eqs. (4) and (5) as follows. Stronger electron-releasing effect of *i*-propyl group on the carbon atom of the C–Sn bond is balanced by the substitution of two haloacyloxy groups of strong electron-withdrawing property. In contrast, less electron-releasing effect of *n*-propyl group is sufficient to undergo substitution by only one haloacyloxy group. Alkyl group in (2-acetoxyethyl)-trialkyltin, $R_3SnCH_2CH_2OCOCH_3$, seems to make the adduct susceptible to the decomposition in contrast to phenyl group. In this respect *n*-butyl group is more electron-releasing than ethyl group. Thus, adduct **4** is concluded to be more susceptible than **3**.

Experimental

All melting and boiling points are uncorrected. The IR spectra were obtained by a Perkin-Elmer 221 spectrometer. The NMR spectra were recorded by a Japan Electron Optics 3H-60 spectrometer, using a tetramethylsilane as an internal standard.

Materials. Tri-*n*-butyltin and triethyltin hydrides were prepared by reduction of tri-*n*-butyltin and triethyltin chlorides with lithium alminum hydride,[7] respectively, and distilled just before use. Triethyltin chloride was prepared by disproportionation of tetraethyltin and tin tetrachloride.[8] Commercial products of tri-*n*-butyltin chloride, tin tetrachloride, allyl acetate, vinyl acetate, and ethyl acrylate were used.

Irradiation. An unsaturated ester (0.01 mol), after being degassed by four freeze-thaw processes, was transferred by a vaccum line into an ampul containing degassed trialkyltin hydride (0.01 mol). The ampul, after being fused, was irradiated at room temperature with γ-rays from a ^{60}Co source without agitation.

Separation and Identification of the Products. Gas chromatography was carried out with a Yanagimoto GCG-5DH fitted with a FID detector, using a 2m column containing 25% Silicone DC-200 on Celite 545.

Run 1. The irradiated product was determined by glpc and identified[9] by IR and NMR in a carbon tetrachloride solution. IR (CCl_4): 2950, 2915, 1740, 1450, 1375, 1228, and 1020 cm^{-1}; NMR (CCl_4): δ 4.09 (q, 2H, CH_2), δ 2.47 (t, 2H, CH_2), δ 1.8—0.5 (m, 32H, CH_2 and CH_3).

Run 2. The reaction product was determined by glpc. For identification the product was distilled *in vacuo*, the frac-

---

[3] G. J. M. van der Kerk and J. G. A. Luijten, *J. Appl. Chem.*, **6**, 49 (1956).

[4] (2-Acetoxyethyl)-triethyltin was reported to decompose at 70—80°C to yield ethylene and quantitative amount of triethyltin acetate; W. P. Neumann, H. Niermann, and R. Sommer, *Ann. Chem.*, **659**, 27 (1962), and reference therein.

[5] J. G. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 356 (1957).

[6] G. S. Sasin, A. L. Borror, and R. Sasin, *J. Org. Chem.*, **23**, 1366 (1958).

[7] G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 366 (1957).

[8] K. A. Kozeschkow, *Ber.*, **66**, 1661 (1933).

[9] M. Pereyre, G. Colin, and J. Valade, *Bull. Soc. Chim. Fr.*, **1968**, 3358.

tion boiling at 95—100°C/0.001 mmHg being collected. IR (CCl_4): 2950, 2915, 1737, 1450, 1370, 1365, 1233, and 1030 cm^{-1}; NMR (CCl_4): δ 3.94 (t, 2H), δ 2.00 (s, 3H), δ 1.8—0.5 (m, 31H, CH_2 and CH_3).

Run 3. Distillation gave the product boiling at 70—80°C/0.001 mmHg: n_D^{20} 1.4750 (lit,[4]) 1.4773). IR (CCl_4): 2950, 2915, 2815, 1740, 1390, 1240, 1055, 1025, and 970 cm^{-1}.

Run 4. A mixture of 1 : 2 molar ratio gave after irradiation curdy products, which were filtered and reprecipitated with petroleum ether from benzene. IR (film): 2950, 1730, 1370, 1240, and 1025 cm^{-1}. In the case of equimolar ratio, tri-*n*-butyltin acetate precipitated in the irradiated mixture was filtered and recrystallized from petroleum ether. IR (KBr): 2950, 2915, 2850, 1575, 1550, 1405, 1340, and 670 cm^{-1}; NMR (CCl_4): δ 1.96 (s, 3H, CH_3), δ 1.8—0.7 (m, 27H, CH_2 and CH_3). Found: C, 47.68; H, 8.82%. Calcd for $C_{14}H_{30}O_2Sn$; C, 48.16; H, 8.66%.

Gas Analysis. Evolution of ethylene from the decomposition of adduct **4** was confirmed as follows. The sample tube fitted with a breakable seal was attached to a vacuum line and the seal was broken. The products noncondensable at −196°C were determined by the Toepler gauge, and analyzed by mass spectrometry (Hitachi RMU-5G) and gc (Hitachi KGL-2A) on a molecular sieves column with N_2 as carrier. The condensable fraction was vaporized with a dry ice-acetone bath, and analyzed by gc using a silica gel column. Ethylene (0.045 mol), *n*-butane (0.009 mol) and hydrogen (0.005 mol) were found. However, tri-*n*-butyltin hydride irradiated under similar conditions gave *n*-butane (0.005 mol) and hydrogen (0.008 mol). Thus, in the case of the decomposition of adduct **4**, *n*-butane and hydrogen can be formed from the irradiation of the starting material (tri-*n*-butyltin hydride) and not from the decomposition of adduct **4**.