followed by dilution with water after the reaction mixture had been kept for 30 min at room temperature, gave pinkish prisms, mp 129–130° from methanol. *Anal.* Found: C, 39.4; H, 2.2; N, 7.2. The structure of this bromide derivative of **4a** is under investigation; however, it is presumed that a vinyl bond and a phenyl ring have been brominated, the latter in the *para* position.

Registry No.—4a, 21232-58-6; **4b**, 22538-42-7.

γ-Induced Addition of Trichlorosilane to Vinyl Acetate

Jitsuo Tsurugi, Ren Nakao, and Tsugio Fukumoto

*Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka, Japan*

Addition of trichlorosilane to a number of olefinic double bonds has been reviewed.[1] However, very little is known about the addition to an olefinic double bond adjacent to an acetoxy group. Only a short description[2] has been given that trichlorosilane added to vinyl acetate by benzoyl peroxide, giving the 1:1 adduct, 2-trichlorosilylethyl acetate, in 15% yield, based on vinyl acetate. The present note will report γ-induced addition of the same system, conversion of the trichlorosilyl group of the 1:1 adduct to the triethoxysilyl group, and subsequent pyrolytic loss of acetic acid from the 1:1 adduct and its triethoxylated compound. The above three steps may lead to synthesis of vinyltrichloro- and vinyltriethoxysilane starting from trichlorosilane and vinyl acetate, although other processes have been utilized for synthesis of vinyltrichlorosilane[3-6] and vinyltrialkoxysilanes.[7]

A mixture of trichlorosilane and vinyl acetate in a fused tube was irradiated with a ⁶⁰Co source. Distillation of the irradiated mixture yielded three fractions, two boiling at 42 and 65° (6 mm), respectively, and residue [>70° (6 mm)]. The lower boiling fraction was identified as 2-trichlorosilylethyl ethyl ether, Cl_3SiCH_2-$CH_2OCH_2CH_3$, by the coincidence of physical constants with those reported,[8] and confirmed further by conventional methods, especially by nmr. The higher

(1) F. W. Stacey and J. F. Harris, Jr., *Org. Reactions*, **13**, 209 (1963).
(2) M. F. Shostakovskiĭ and L. I. Shomonina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 64 (1958).
(3) From chloroalkyltrichlorosilane by dehydrochlorination: A. D. Petrov, V. A. Ponomarenko, B. A. Sodolov, and Yu. P. Egorov, *ibid.*, 310 (1957); R. Müller and K. Schnurrbusch, *Chem. Ber.*, **91**, 1805 (1958).
(4) From vinyl chloride by Si-containing catalysts: D. T. Hurd, *J. Amer. Chem. Soc.*, **67**, 1813 (1945); A. L. Klebanskiĭ and V. S. Fikhtengol'ts, *Zh. Obshch. Khim.*, **27**, 2648 (1957); M. F. Shostakovskiĭ, E. M. Savitskiĭ, D. A. Kochkin, and L. V. Musatova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1493 (1957).
(5) From acetylene and trichlorosilane: G. H. Wagner and C. O. Strother, British Patent 670,617 (1952); M. F. Shostakovskiĭ and D. A. Kochkin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1150 (1956).
(6) From vinyl chloride and trichlorosilane: British Patent 752,700 (1956).
(7) Alkoxylation of vinyltrichlorosilane: R. Nagel, C. Tamborski, and H. W. Post, *J. Org. Chem.*, **16**, 1768 (1951).
(8) R. Clalas, N. Duffaut, and J. Valade, *Bull. Soc. Chim. Fr.*, 790 (1955).

boiling one was identified as the 1:1 adduct, 2-trichlorosilylethyl acetate. The residue gave, after three distillations, a fraction boiling at a range of 113–115° (3 mm), which was identified as the 1:2 adduct, 4-trichlorosilyl-3-acetoxybutyl acetate, $Cl_3SiCH_2CH(OAc)$-CH_2CH_2OAc. To exemplify our assumption that the ether arose from reduction of the 1:1 adduct under the present conditions, a mixture of the 1:1 adduct and trichlorosilane (the molar ratio of which 1:6) was irradiated under a total dose of 10 MR at a dose rate of 0.6 MR/hr. Distillation of the irradiation mixture gave 2-trichlorosilylethyl ethyl ether in 67% yield, based on the 1:1 adduct. Equation 1 represents a

$$Cl_3SiCH_2CH_2OCOCH_3 \xrightarrow{HSiCl_3} Cl_3SiCH_2CH_2OCH_2CH_3 \quad (1)$$
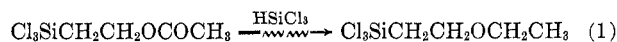
quite novel reaction indicating reduction of a carbonyl to methylene. If it is true, we can expect to reduce a carboxylic ester in general to an ether by this method. In fact, alkyl aliphatic carboxylates, methyl, ethyl, and *n*-propyl esters of formic, acetic, and propionic acids so far studied, could be reduced to the corresponding dialkyl ethers. Trichlorosilane, in turn, changed to hexachlorodisiloxane. RCOOR', of which either R or R' is aryl or aralkyl, could not be reduced, however. The scope and sequence of this reduction will be reported elsewhere.[9]

After identification of the fractions obtained from the irradiated mixture, the effects of irradiation dose rate, total dose, and molar ratio of the silane to vinyl acetate on the yield of the 1:1 adduct were studied, and are shown in Tables I, II, and III, respectively. Table III shows that when the molar ratio is lower, the amount of the residue is greater. This result can be explained by a radical chain telomerization mechanism, that is, competition of the chain transfer step by the silane with the chain propagation step to vinyl acetate. The proportion of either step depends on the molar ratio of the mixture. Table III also indicates that, as the molar ratio increases above 8, the amount of ether increases at the expense of the 1:1 adduct. This result can be ascribed to eq 1. Other investigators[10] reported that γ-induced addition of trichlorosilane to an alkene like 1-octene occurred almost quantitatively. The better yield for the simple olefin in contrast to the yield for vinyl acetate can be explained by the facts that the simple alkene does not form 1:2 or higher adducts and that the 1:1 adduct produced does not change during the reaction. The same investigators[10] also reported that trichlorosilane added to allyl acetate by γ irradiation, giving 1:1 and 1:2 adducts in 22 and 71% yield, respectively, based on alkene. In this case, the molar ratio of silane to alkene was 3. Therefore, reduction of the adducts by the silane seems not to predominate, as the total yield indicates. Our results given in Table III also indicate that no reduction occurs with this molar ratio.

Since the trichlorosilyl group is, as is well known,[10] sensitive even to atmospheric moisture, it seems necessary to convert this group to a stable one for further treatments. Although alkylation by the Gri-

(9) J. Tsurugi, R. Nakao, and T. Fukumoto, *J. Amer. Chem. Soc.*, **91**, 4587 (1969).
(10) A. M. El-Abbady and L. C. Anderson, *ibid.*, **80**, 1737 (1958).

TABLE I

The Product Distribution and Dose Rate at a Given Molar Ratio[a] under a Given Total Dose[b]

Dose rate, MR/hr	Consumed amount of TCS, g	Cl₃SiCH₂CH₂OCH₂CH₃	Cl₃SiCH₂CH₂OCOCH₃[c]	Residue, g
		Products, g		
0.010	13.0	2.6	7.0 (36.5, 32.8)	3
0.025	10.7	0.3	8.5 (43.8, 48.4)	3
0.075	10.1	1.1	7.8 (40.2, 47.0)	2.5
0.20	10.5	0.6	10.0 (51.1, 58.1)	4
0.60	10.0	0	9.5 (48.8, 58.0)	3

[a] TCS/VAc = 4.0. Starting amounts of TCS (trichlorosilane) and VAc (vinyl acetate) are 47.1 and 7.5 g, respectively. [b] Total dose = 0.6 MR. [c] Figures in parentheses indicate yields (%) based on VAc and on consumed amount of TCS, respectively.

TABLE II

The Product Distribution and Dose at a Given Molar Ratio[a]

Dose rate MR/hr	Total dose, MR	Consumed amount of TCS, g	Cl₃SiCH₂CH₂-OCH₂CH₃	Cl₃SiCH₂CH₂OCOCH₃[b]	Residue, g
			Products, g		
0.20	0.10	1.9	0	0 (0, 0)	2.5
0.20	0.30	13.5	0	5.3 (37.4, 24.0)	2
0.20	0.60	14.0	0	6.9 (48.7, 30.1)	3
0.20	1.2	15.5	0.8	6.1 (43.1, 24.1)	3
0.30	4.8	20.7	4.1	3.5 (24.7, 10.3)	2

[a] TCS/VAc = 4.6. Starting amounts of TCS (trichlorosilane) and Vac (vinyl acetate) are 40.3 and 5.5 g, respectively. [b] See footnote c of Table I.
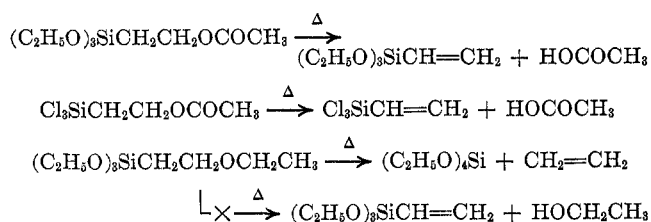
TABLE III

The Product Distribution and Molar Ratio under a Given Dose (0.60 MR) and Dose Rate (0.20 MR/Hr)

Starting molar ratio (TCS/VAc)[a]	Starting amount of TCS, g	Consumed amount of TCS, g	Cl₃SiC₂H₄OCH₂CH₃	Cl₃SiCH₂CH₂OCOCH₃[b]	Residue, g
			Products, g		
1	20.0	18.2	0	9.0 (27.3, 30.1)	13.5
2	26.2	15.1	0	9.2 (42.8, 36.6)	10
3	30.3	11.0	0	9.3 (56.0, 50.6)	8
4	32.3	9.9	1.5	8.7 (65.7, 53.5)	3
6	34.6	8.6	1.0	6.5 (67.8, 46.0)	3
8	36.3	7.6	2.6	4.6 (61.7, 36.9)	3
10	40.4	7.5	3.2	4.1 (61.7, 33.2)	3

[a] TCS (trichlorosilane), VAc (vinyl acetate). [b] See footnote c of Table I.

gnard[11] method may be possible, alkoxylation[7,12] was attempted here. Ethanolysis of the 1:1 adduct gave 2-triethoxysilylethyl acetate in 83% yield. Our attempts for direct addition of triethoxysilane to vinyl acetate induced by γ irradiation failed. This may be ascribed to less radical susceptibility of hydrogen in the triethoxy compound compared with the greater one of trichlorosilane.[13]

Pyrolysis of 2-triethoxysilylethyl acetate and 2-trichlorosilylethyl acetate at 550° by a modified Bailey method[14] gave vinyltriethoxysilane in 82.5% yield and vinyltrichlorosilane in 71.7% yield, respectively. However, 2-triethoxysilylethyl ethyl ether gave tetraethoxysilane in 64.5% yield on pyrolysis, contrary to our expectation of vinyl triethoxysilane and ethanol.

$$(C_2H_5O)_3SiCH_2CH_2OCOCH_3 \xrightarrow{\Delta} (C_2H_5O)_3SiCH=CH_2 + HOCOCH_3$$

$$Cl_3SiCH_2CH_2OCOCH_3 \xrightarrow{\Delta} Cl_3SiCH=CH_2 + HOCOCH_3$$

$$(C_2H_5O)_3SiCH_2CH_2OCH_2CH_3 \xrightarrow{\Delta} (C_2H_5O)_4Si + CH_2=CH_2$$

$$\mathsf{L}_{\times} \xrightarrow{\Delta} (C_2H_5O)_3SiCH=CH_2 + HOCH_2CH_3$$

(11) J. J. Eisch and J. T. Trainor, _J. Org. Chem._, **28**, 487 (1963).

(12) S. H. Langer, S. Connell, and I. Wender, _ibid._, **23**, 50 (1958).

(13) J. A. Kerr, D. H. Slater, and J. C. Young, _J. Chem. Soc., A_, 104 (1966); 134 (1967).

(14) W. J. Bailey and L. Nicholas, _J. Org. Chem._, **21**, 648 (1956); F. Mashio, private communication.

Experimental Section

Reagents and Procedures of Identification.—All boiling points described are uncorrected. Precautions were taken to ensure dry conditions during distillation and subsequent treatments of trichlorosilane and the products containing the trichlorosilyl group. Commercial trichlorosilane was distilled at 32° in a stream of nitrogen. Other reagents were commercial ones used without further purification. Triethoxysilane was prepared from trichlorosilane and absolute ethanol by the method of Volkov, et al.[15]

Elemental analysis was carried out by Yanagimoto CHN Corder. Chlorine contents in the trichlorosilyl group were determined by the method of Sommer.[16] Ir spectra were taken with a Perkin-Elmer Model 221, and nmr spectra on a JNM 3H-60 with tetramethylsilane as an internal standard. Molecular weights were determined by Hitachi Perkin Elmer 115 with benzene as a solvent.

Procedure for Irradiation.—A given mixture was degassed by three thawings and freezings at −190° and transferred directly from a bulb to a glass tube by a vacuum line. The tube, after being fused, was irradiated by γ rays from an 8000-Ci ⁶⁰Co source at room temperature.

γ-Induced Addition of Trichlorosilane to Vinyl Acetate.—After irradiation of the mixture, unchanged trichlorosilane was recovered. Distillation (6 mm) yielded three fractions.

A fraction boiling at 42° (6 mm) was identified as 2-trichlorosilylethyl ethyl ether by the following determinations: bp 146° (760 mm) [lit.[8] 146–147° (764 mm)]; ir 1110 cm⁻¹ (C–O–C); nmr (CCl₄) δ 1.18 (t, 3, J = 12 Hz, CH₃), 1.79 (t, 2, J = 11 Hz, Si–CH₂), 3.5 (m, 4). Absorption at ca. δ 3.5 consisted of two

(15) V. L. Volkov, M. I. Kafyrov, S. I. Kleshchevnikova, and E. I. Rumyantseva, _Plast. Massy_, 28 (1962); _Chem. Abstr._, **59**, 1469c (1963).

(16) L. H. Sommer, E. Dorfman, G. M. Goldberg, and F. C. Whitmore, _J. Amer. Chem. Soc._, **68**, 488 (1946).

superimposed signals, one triplet and another quartet, which proved to be coupled with the counterparts of methyl or methylenic signals in the higher field, by double-resonance methods. Namely, when the triplet of methyl at δ 1.18 was irradiated ($\Delta\omega$ = 134.3 cps), the quartet at δ 3.47 coalesced, and, when the triplet of methylene at δ 1.79 was resonated, the triplet at δ 3.37 again changed into a singlet. *Anal.* Calcd for $Cl_3SiC_4H_9$: Cl, 51.3; Si, 13.5. Found: Cl, 51.0; Si, 14.0. This compound was again identified after being converted to 2-triethoxysilylethyl ethyl ether.

A fraction boiling at 65.5° (6 mm) was identified as 2-trichlorosilyl ethyl acetate (1:1 adduct): bp 65.5° (6 mm) [lit.[2] 64.5–66.5° (6 mm)]; n^{20}D 1.4454; ir 1745 (C=O), 1230 cm^{-1} (C–O). *Anal.* Calcd for $Cl_3SiC_4H_7O_2$: Cl, 48.01; Si, 12.68. Found: Cl, 48.31; Si, 12.56.

Distillation residues (>70° (6 mm)) of several runs were collected. Distillation (3 mm) of the collected residues (100 g) indicated decomposition slowly occurring, but gave 21 g of a fraction (110–130°) and 17 g of lower boiling fraction which could not be identified. Two distillations of the higher boiling fraction at 2 mm gave 15 g of a fraction boiling at 113–115° (2 mm) which was identified as 4-trichlorosilyl-3-acetoxybutyl acetate (1:2 adduct): ir 1745 (C=O), 1230 cm^{-1} (C–O). *Anal.* Calcd for $Cl_3SiC_8H_{13}O_4$: Cl, 34.62; Si, 9.13. Found: Cl, 33.74; Si, 9.03.

γ-Induced Reduction of 2-Trichlorosilylethyl Acetate.—A mixture of 2-trichlorosilylethyl acetate (11.1 g, 0.05 mol) and trichlorosilane (40.6 g, 0.3 mol) was irradiated under total dose of 9.6 MR at a dose rate of 0.6 MR/hr. Distillation of the irradiated products, after the removal of the unchanged trichlorosilane, gave 6.9 g (0.033 mol, 67%) of 2-trichlorosilylethyl ethyl ether. The boiling point and ir and nmr spectra coincided completely with those cited above.

Triethoxylation of the Trichlorosilyl Group.—The ethanolysis was carried out by the modified procedure of Nagel, *et al.*,[7] and Langer.[12] A mixture of ethanol (25 g, 0.54 mol) and pyridine (90 g, 1.17 mol) added to 2-trichlorosilylethyl acetate (33.7 g, 0.152 mol) gave 2-triethoxysilylethyl acetate (26.9 g, 71%): bp 90.6° (3.5 mm); n^{20}D 1.4109; ir 1745 (C=O), 1230 (C–O). *Anal.* Calcd for $SiC_{10}H_{22}O_5$: Si, 11.22; C, 47.97; H, 8.86; mol wt, 250.4. Found: Si, 11.45; C, 48.03; H, 9.36; mol wt, 243.5.

A mixture of ethanol (16.0 g, 0.348 mol) and pyridine (60 g, 0.758 mol) with 2-trichlorosilylethyl ethyl ether (21.0 g, 0.101 mol) yielded 2-triethoxysilylethyl ethyl ether (19.8 g, 83%): bp 75.5° (6 mm); n^{20}D 1.4067. *Anal.* Calcd for $SiC_{10}H_{24}O_4$: Si, 11.88; C, 50.81; H, 10.23; mol wt, 236.4. Found: Si, 11.88; C, 51.63; H, 10.04; mol wt, 236.

Attempted Addition of Triethoxysilane to Vinyl Acetate.—A mixture of triethoxysilane (26.3 g, 0.16 mol) and vinyl acetate (3.45 g, 0.04 mol) was γ irradiated under a total dose of 0.6 MR, at a dose rate of 0.2 MR/hr. 2-Triethoxysilylethyl acetate could not be found by distillation.

Pyrolysis.—2-Triethoxysilylethyl acetate (9.9 g, 0.0395 mol) was vaporized and made to flow under 1 mm of pressure through a Pyrex reactor (*ca.* 20-cm path) packed with Pyrex helices and externally heated at 550°, in a stream of nitrogen.[14] The pyrolysates were collected in two traps cooled in an ice and a liquid nitrogen bath. The content of the latter trap was dissolved in ether and washed with water, aqueous sodium bicarbonate, and then water. The ether solution gave 6.2 g (0.326 mol, 82.5%) of vinyltriethoxysilane, the boiling point and n^{20}D coincided with those[17] reported, and the ir and nmr spectra matched those of a commercial sample. *Anal.* Calcd for $SiC_8H_{18}O_3$: C, 50.49; H, 9.53; mol wt, 190. Found: C, 49.62; H, 10.26; mol wt, 186.

2-Trichlorosilylethyl acetate (10.4 g) was pyrolyzed by the same procedure. An aliquot of a fraction trapped with liquid nitrogen, after distillation, gave vinyltrichlorosilane; the physical properties (boiling point, n^{20}D, and nmr spectrum) coincided with those reported.[3,18] The remaining part of the fraction was analyzed by glpc using vinyltrichlorosilane obtained above as a standard. Considering the unchanged amount (2.5 g) of the starting acetate, pyrolysis yielded 71.7% vinylsilane.

2-Triethoxysilylethyl ethyl ether (6.0 g, 0.0254 mol) was pyrolyzed. A fraction trapped with liquid nitrogen was identified

to be ethylene by glpc. The other fraction was distilled, giving tetraethoxysilane (3.4 g, 0.0167 mol, 64.5%): bp 82–83° (30 mm) and 161.3° (760 mm) [lit.[19] 165.5° (760 mm)]; nmr (CCl₄) δ 1.21 (t, 3, J = 12 Hz, CH₃), 3.72 (q, 2, J = 12 Hz, CH₂). *Anal.* Calcd for $SiC_8H_{20}O_4$: C, 46.12; H, 9.68; Si, 13.45. Found: C, 46.39; H, 10.32; Si, 13.85.

Registry No.—Trichlorosilane, 10025-78-2; vinyl acetate, 108-05-4; 4-trichlorosilyl-3-acetoxybutyl acetate, 22538-44-9; 2-triethoxysilylethyl acetate, 22538-45-0; 2-triethoxysilylethyl ethyl ether, 17980-59-5.

(19) "Beilstein, Handbuch der Organischen Chemie," Vol. 1, 1918, p 334.

Potentially Tautomeric α-(2-Benzimidazolylthio)acetophenones

HOWARD ALPER AND ANNE E. ALPER

*Department of Chemistry
State University of New York at Binghamton,
Binghamton, New York 13901*

Ring–chain tautomeric investigations have shown 3-hydroxy-2,3-dihydrothiazolo[3,2-*a*]benzimidazoles unsubstituted on the thiazolidine ring (as well as the 2-methyl compound) to exist only as the cyclic carbinolamines, both in the solid state and in solution.[1] 3-Hydroxy-3-methyl-2,3-dihydrothiazolo[3,2-*a*]benzimidazole also exists as the ring tautomer (Ia) in the solid state (infrared studies using potassium bromide disks), but nmr spectra of dimethyl sulfoxide-d_6 (DMSO-d_6) solutions have clearly indicated the presence of a 1:2 mixture of Ia and the open-chain amino ketone tautomer Ib, respectively. α-(2-Benzimidazolylthio)acetophenone (II, X = H), on the other hand, exists solely
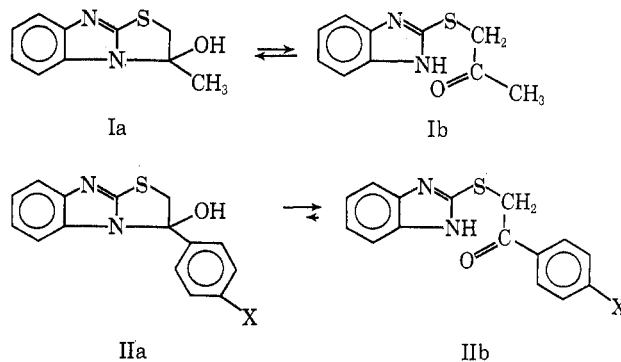
in the chain form IIb, both in the solid state and in solution. As the 3-methyl compound Ia is in tautomeric equilibrium with Ib in solution, it seemed conceivable that IIb, appropriately substituted, would be capable of interconverting with the cyclic tautomer IIa. This communication reports an investigation of the influence of a *para* substituent on the position of the ring–chain tautomeric equilibrium IIa ⇌ IIb.

(1) A. E. Alper and A. Taurins, *Can. J. Chem.*, **45**, 2903 (1967).

(17) R. Y. Mixer and D. L. Bailey, *J. Polym. Sci.*, **18**, 573 (1955).

(18) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 3.